HANDBOOK
OF
CHEMICAL ENGINEERING

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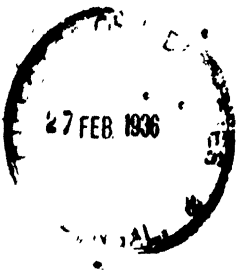
PREPARED BY A STAFF OF SPECIALISTS

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"METALLURGIST AND CHEMISTS' HANDBOOK," EDITOR "HANDBOOK
OF NON-FERROUS METALLURGY"

IN TWO VOLUMES
VOL. II

FIRST EDITION
FIFTH IMPRESSION

McGRAW-HILL BOOK COMPANY, INC.
NEW YORK: 370 SEVENTH AVENUE
LONDON: 6 & 8 BOUVERIE ST., E. C. 4
1922



660.02
L 619

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PRINTED IN THE UNITED STATES OF AMERICA

2040

THE MAPLE PRESS - YORK PA

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HANDBOOK OF CHEMICAL ENGINEERING

SECTION XIV

HIGH TEMPERATURE PRODUCTION

By Colin G. Fink[1]

A Modern Art.—One of the most distinctive features of modern metallurgy as compared with that of two or three generations ago is the ease with which temperatures of 2,000 to 4,000°C. are attainable by means of comparatively simple apparatus. Metals such as platinum, tantalum and tungsten, or compounds such as lime, magnesia or alumina, heretofore rated as infusible are today readily melted. Pure magnesia melts at 2,240°, pure tungsten at 3,260°C.

Not only have these high temperatures been brought about by the introduction of the electric arc, but great strides have been made in the better utilization of the heating value of carbonaceous fuels. Furthermore, the introduction of the art of aluminothermics has made it comparatively simple to produce metals and alloys at 3,000°C., metals and alloys which heretofore could not be produced as readily and as cheaply and as free from carbon by any other process

Before proceeding to outline briefly the various heating methods employed in bringing about high temperature melting or reactions, we shall refer in a few words to the subject of refractories for high-melting-point containers.

High-temperature Refractories.—Our choice of materials is very limited especially for temperature work in excess of 2,000°C. Of the various refractories readily obtainable, lime, magnesia and alumina are the most serviceable basic ones at temperatures up to about 1,900°. The purer these oxides the higher their melting points. In laboratory tests thoria crucibles have given very satisfactory results at temperatures as high as 2,400°C. Although pure tungsten melts at 3,260°C., crucibles made from this metal, unless constructed with very heavy walls, show marked tendency to collapse at about 2,800°C. In those cases where carbon does not readily combine with the substance to be heated, commercially pure graphite crucibles or supports are serviceable up to temperatures of about 3,000°C. The life of these graphite crucibles at these elevated temperatures is however comparatively short since the amorphous carbon binder used in the manufacture of the crucible rapidly loses its binding qualities as the graphitization temperature is approached.

At the maximum temperatures of 3,000 to 4,000°C. commercially obtainable there is, aside from carbon, no metal or compound known that will serve as lining or crucible material for protracted heating. When operating at these extreme temperatures resource is had to various special methods which can best be described by citing a few definite examples. In order to melt pure tungsten metal into a solid coherent form the practice today consists in compressing metallic tungsten powder into rod or ingot form and then after a preliminary sintering connecting the ends to an electric low-voltage, high-current terminal and passing enough current through the rod or ingot to bring its temperature to almost the melting point. This operation is carried out in an atmosphere of hydrogen or ammonia in order to avoid oxidation of the metal. Another

[1] Consulting electrometallurgist, New York, N. Y.

method, which is commercially applied to melting tantalum into buttons or ingots consists in playing an arc between a compressed tantalum rod vertically suspended and a small base of fused tantalum and allowing the metal globules, as they descend from the upper electrode, to collect and build up into a button or rod. The operation is carried out in vacuum on account of the marked tendency of tantalum to combine with all of the ordinary gases.

Of particular interest on account of the increasing wide application is the aluminothermic or Goldschmidt method of attaining temperatures of 3,000°C. and above. The success of the process is largely dependent upon the speed with which the entire melting operation is carried out. Only a few minutes or seconds suffice to complete the reaction and during this short time the magnesite lining of the pot does not reach its melting point which is 1,000° below that of the reaction temperature. In place of aluminum metal, magnesium-aluminum alloy or rare earth metals may be used. Carbon-free ferro-vanadium, chromium and manganese metals are made exclusively by Goldschmidt's method.

Oxyacetylene Flame.—The temperature of the oxyacetylene flame is approximately 3,500°C. This flame, as is well known, has a wide application in the welding and cutting of iron and steel. Its use for melting metals and compounds is rather limited on account of the marked tendency for the material being heated to take up carbon.

Oxyhydrogen Flame.—The oxyhydrogen flame is well suited for the melting of platinum and other precious metals. It is also used extensively in fusing and working quartz and for fusing oxide of aluminum in the manufacture of synthetic rubies and amethysts. The temperature of the flame is about 2,000°C.

Oxywater-gas Flame.—For the working of high-fusing glass such as Pyrex, the oxywater-gas flame is very serviceable. The temperature of the flame is several hundred degrees lower than that of the oxyhydrogen flame and therefore will not melt platinum nor quartz.

Surface Combustion.—Although the phenomenon of surface combustion had been observed and studied for a good many years, it was not until the beginning of this century that the underlying principles were adapted in commercial burners and heating apparatus. The practical success of surface combustion is largely due to W. A. Bone[1] and there are a large number of welding furnaces, glass-melting furnaces, oil-cracking, carbonizing and heat-treating furnaces in use today constructed on the "Bonecourt" system.

In surface combustion "a homogenous explosive mixture of gas and air, in the proper ratio for complete combustion is caused to burn without flame in contact with a granular incandescent solid, whereby a large proportion of the potential energy of the gas is immediately converted into radiant form." One of the most familiar cases of surface combustion is the Welsbach incandescent gas mantle. The temperature of this mantle under favorable conditions is as high as 2,300°C. whereas in the ordinary Bunsen gas flame it is difficult to attain a temperature of 1,800°C. We are dealing here with contact catalysis. As early as 1834 Faraday advanced the theory that the function of the surface was to condense both the oxygen and the combustible gas, "thus producing in the surface layers a condition comparable to that of high pressure." In Bone's early experiments (1902)[2] he showed that (1) the power of accelerating gaseous combustion is possessed by all surfaces at temperatures below the

[1] *Proc.* Roy. Inst. Great Britain, Vol **21**, pp. 41–62, 1914, *Engineering*, Vol. **91**, p. 487, 1911; *Journ* Franklin Inst. Vol. **173**, p. 101, 1912; *Journ.* Soc. Chem. Ind. Vol. **38**, p. 228 T, 1919.

[2] *Proc.* Roy. Inst. Great Britain *l. c.*

ignition point; (2) such an accelerated surface combustion is dependent upon an absorption of the combustible gas and probably also of the oxygen, by the surface, whereby it becomes activated by association with the surface; and (3) the surface itself becomes electrically charged during the process. Bone contended "that if hot surfaces possess the power of accelerating gaseous combustion at temperatures *below* the ignition point, the same power must also be manifested in even a greater degree at *higher* temperatures and especially so when the surface itself becomes incandescent." J. J. Thomson suggested that the emission of electrons or charged particles from the incandescent surface was a factor of primary importance

The contact material may be a porous firebrick, granular quartz, granular alumina, etc. Platinum is easily melted in a surface combustion furnace using ordinary coal gas. In Bone's high temperature test furnaces pure alumina can be fused. The advantages claimed for the Bonecourt surface combustion system are: (1) The combustion is greatly accelerated by the incandescent surface and if so desired may be concentrated just where the heat is required; (2) the combustion is perfect with a minimum excess of air, (3) the attainment of very high temperatures is possible without the aid of elaborate regenerative devices; and (4) owing to the large amount of radiant energy developed, transmission of heat from the seat of combustion to the object to be heated is very rapid For many important industrial heating applications surface combustion is not only "pre-eminently economical but also easy of control. With coal gas or water gas, without regeneration, temperatures of 1,900 to 2,000°C. are attained, with heat recuperation, still higher temperatures are attained.[1]

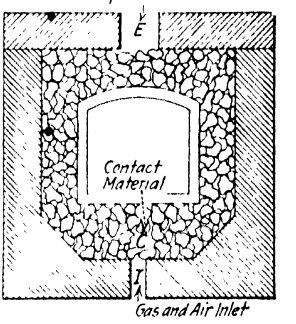


FIG. 1.—Surface-combustion unit.

Fuel Oil Furnaces.[2] The fuel oil is sprayed into the furnace by means of an atomizer or burner which pulverizes the oil and delivers it in a gaseous vapor or in small globules at the hottest place in the furnace. Air is admitted from below and as soon as the temperature is raised to the ignition point, chemical reaction takes place with the atomized fuel oil and thus heat is generated. The heat is absorbed by the gases of the furnace and consequently their temperature is at once raised oftentimes to 1,200 to 1,500°C. These furnace gases consist of the inert nitrogen that partly constituted the entering air, the carbon dioxide or carbon monoxide formed by the burning of the carbon, water vapor formed by the burning of the hydrogen, sulphur dioxide formed by the burning of the sulphur content, which latter ingredient is always small and a considerable quantity of free oxygen depending on the amount of excess air admitted to the furnace.

Colloidal Fuel.[3]—Colloidal fuel is a combination of liquid hydrocarbon with finely pulverized carbonaceous substance, the components so combined and so

[1] Additional references A. E. Blake, in Bacon & Hamor's "American Fuels," McGraw-Hill, 1921; W. D. Bancroft, *Jour. Physic. Chem.*, Vol. **21**, p. 641, 1917; Carleton Ellis, *Trans.* A. I. M. E., Vol. **43**, p. 612, 1912

[2] "Fuel Oil and Steam Engineering" by Robert and C. H. Delany, McGraw-Hill, 1921.

[3] An abstract of a detailed report by Landon W. Bates, *Canadian Chem. Jour.*, Vol. **4**, p. 40, 1920, *cf.* also, "Reports of the Submarine Defence Association" by L. W. Bates, S. E. Sheppard, and Haylett O'Neill.

treated as to form a stable fuel capable of being atomized and burned in a furnace. It is made in three forms, a liquid, a gel and a mobile paste. The name "colloidal" is not scientifically exact since only part of the carbon present is in the colloidal form. On the other hand the title is descriptive since the composite possesses many important colloid-like characteristics. The proportions are usually 60 per cent oil and 40 per cent coal. Up to ratios of 25 per cent oil and 75 per cent coal the fuel is a mobile paste. All kinds of oils and solid carbons may be used. The cheap coal wastes and breakages are all available. The "colloidal fuel" is used in the selfsame way as oil fuel and with the same apparatus. In general colloidal fuel is on a parity with oil, while certain grades are superior.

In marine tests on the U. S. S. "Gem," equipped with Normand express boilers, colloidal fuel evaporative efficiency reached 91.5 per cent on a short run, while that of the Navy oil did not on any run exceed 79.4 per cent and that of pulverized coal 72.6 per cent. The calorific value per unit volume is greater than that of straight oil. For example, in a composite made up of 35 per cent by weight of pulverized coal of 14,000 B.t.u. per pound and 1.6 specific gravity, and 65 per cent oil of 18,200 B.t.u. per pound, 0.96 specific gravity, a gallon of the composite has 165,000 B.t.u. while oil has 146,000 B.t.u. per gallon. Colloidal fuel is heavier than water while oil is lighter; colloidal fuel may be stored under a water seal and its fire may be quenched with water. The gel is easily changed to the liquid form by heating. (See also p. 789).

Electric Furnaces.—The advantages of electric furnaces over fuel-fired furnaces are: Ease of control of temperature, long life of linings, absence of contaminating sulphur and other impurities found in ordinary fuels, rigid control of composition of charge, ease of attaining very high temperatures in a short time, absence of nitrogen, low losses due to volatilization of zinc and similar metals, etc. Metals and compounds can be manufactured in the electric furnace that cannot be made in a fuel-fired furnace.

There are three distinct types of electric furnaces now in commercial operation: The resistance furnaces, the arc furnaces and the induction furnaces.

The resistor-type electric furnaces in present use employ as resistor element either carbon, a carbide or a metal or alloy. In the manufacture of carborundum from silica and anthracite the charge itself acts as resistor; similarly, in the graphitization of carbon electrodes the electrodes themselves form the resistor.

Of the large capacity electric resistor furnaces, the Baily is one of the most widely used. This furnace is suitable for melting brass, aluminum, copper and bronzes and also used for holding molten ferro-manganese and steel at temperature. The heating element consists of a circular trough of carborundum packed with granulated carbon. By the circular form of the heating element and the shape of the furnace lining a uniform heat is projected by radiation and reflection onto the materials to be melted. The standard sizes are, 50 kw. with 500 lb. hearth capacity, 75 kw. with 750 lb. hearth capacity and 105 kw. with 1,500 lb. capacity. Among the advantages of the Baily furnace are the low zinc losses when melting brass, simplicity of operation, ready renewal of the resistor, absence of any moving parts and low labor cost. On the other hand, like all resistor-type furnaces, the maximum attainable temperature of the Baily is about 2,100°C. as compared with 3,500°C. in the arc furnace and therefore ferro alloys such as ferro-tungsten or ferro-chromium cannot be produced in the Baily.[1]

[1] For details see T. F. Baily, *Trans* Am. Electrochem. Soc., Vol. **40**, 1921; *ibid*, Vol. **36**, p 411, 1919; *ibid*, Vol. **32**, pp. 155-164, 1917, *cf.* also Frank Thornton, *ibid.*, Vol **32**, pp. 141-154, 1917.

Carbon resistor furnaces for laboratory use have been designed by Borchers, Tucker, Fitzgerald, Clawson and others. The highest temperatures are obtained in the Arsem vacuum furnace. Its heater is a graphite helix in an upright position or in another type the resistor consists of grids cut from graphite slabs. The vacuum chamber is made of cast bronze. All joints are made tight by lead gaskets. After charging the furnace, the cover is replaced and the chamber is exhausted. The vacuum pumps are kept in operation during the experiment. The furnace has been installed in a large number of university and research laboratories. It has been found very serviceable in the study of alloys, high melting point determinations, high temperature fractional distillation, etc.[1] The maximum temperature attained in the Arsem furnace is 3,100°C.

Resistance Furnaces with Metal Resistors.—Of the metal resistors commonly used in large furnaces the nickel-chrome alloys such as "nichrome" and "chromel" are the most serviceable on account of their low temperature coefficient and their resistance to oxidation at temperatures as high as 1,200°C. The alloy resistor is in the shape of ribbon or wire and is supported on frames with insulated knobs or hooks. Large furnaces of this type are widely employd for the heat treatment of steel parts, enameling, japanning, etc.

In the laboratory and for small scale operation nickel, platinum, molybdenum and tungsten are very serviceable resistors. Platinum ribbon-wound quartz tubes will operate very satisfactorily up to temperatures of about 1,400 to 1,500°C. At higher temperatures, especially in the presence of reducing gases, the ribbon gradually disintegrates and small platinum crystals will be found in the silica packing surrounding the tube. For low temperatures, say 600 to 800°C., nickel wire or ribbon resists oxidation remarkably well due largely to the adherent film of oxide formed upon first heating. Molybdenum and tungsten wire-wound alundum tube furnaces will operate satisfactorily up to temperatures as high as 1,800°C., but since these two metals will "burn" when heated in air at these temperatures, the tubes are encased in an airtight iron box in which an atmosphere of hydrogen or ammonia is maintained.[2] A very serviceable furnace of this type consists of a 24-in. alundum tube, 1 in. in diameter, wound with 17 ft. of 0 020-in. diameter tungsten wire. The current consumption is from 10 to 17 amp.; a rheostat of about 200 ohms is connected in series across the 220-volt service line. For the determination of melting points of pure metals and alloys, such as nickel, cobalt, iron, copper, etc., this tungsten-hydrogen furnace is to be recommended. To cite but a single illustration, the melting point of cobalt determined in the Arsem vacuum furnace is 1,494°, whereas, in the tungsten-hydrogen furnace the melting point is 1,610°, as repeatedly determined by the writer. This difference is due to the absence of every trace of carbon in the metal in the latter case. For best results the insulator packing between the outer wall of the tube and the inner walls of the iron casing is pure granular aluminum oxide; when operating the furnace at temperatures of 1,500°C. and below pure calcined magnesia is very satisfactory.

For laboratory-scale operations at temperatures above the softening point of alumina or alundum, the tube itself is made of tungsten. A furnace of this type is described by Wartenberg.[3] The tungsten tube is directly connected to the terminals from the transformer. The tube is encased in an airtight box.[4] These tungsten tube furnaces are recommended for carrying out tests at temperatures up to about

[1] W. C. Arsem, *Journ. Ind. Eng. Chem.*, Vol. **2**, pp. 3-9, 1910; "The Electric Furnace," Alfred Stansfield, McGraw-Hill, and General Electric, *Bull.*, No 4898.

[2] For details, see Winne and Dantsizen, *Trans.* Am Electrochem Soc., Vol **20**, p. 287.

[3] *Zeit Elektrochem.*, Vol. **15**, p 876, 1909.

[4] See also Appelberg, U. S. Pat. 953,774, Apr. 5, 1910.

2,500°C. in an atmosphere absolutely free from carbon monoxide or hydrocarbons. Rubies and sapphires can readily be made in the tungsten-tube furnace.

The Electric Arc.—The temperature of the electric arc has been variously estimated at from 2,000 to 6,000°C., but the usually accepted temperature of the ordinary arc is 3,500 to 4,000°C. W. R. Mott[1] has carried out an exhaustive research on the behavior of various elements and compounds in the arc. His apparatus is very simple and inexpensive. Only small quantities of materials are necessary and definite results can be obtained in a very short time. The outstanding feature of the Beck carbon arc is the very high concentration of energy. A current density of over one ampere per square millimeter is obtained and the total crater of the positive carbon reaches a very high temperature. The positive carbon is covered with rare earths. The temperature of the incandescent gas within the positive crater is between 5,000°C. to 5,500°C. (1,000 c.p. per sq. mm. *vs.* 140 c.p. of an ordinary arc[2]). By increasing the gas pressure about the arc up to 22 atmospheres, Lummer of Breslau has raised the temperature to 6,000°C. or very close to that of the sun. The Beck arc is practically applied to high intensity search lights. Another extreme temperature arc is the tungsten arc operated in hydrogen gas. The tungsten arc is commercially applied in the "pointolite," operating in an enclosed atmosphere of argon. The lamp is used for microscope illumination. On a large commercial scale the electric arc is the basis of the electric steel furnaces, such as the Heroult, the Vom Baur, the Snyder furnace, etc.[3] In the Birkeland and Eyde process for the fixation of atmospheric nitrogen, air is passed through an electric arc. The gases are heated to very high temperatures and then rapidly cooled to counteract the tendency of the nitrous acid to dissociate again into its elements.

In using the electric arc for melting or high-temperature heating we can make the material to be heated or melted the lower electrode and use a carbon rod as the upper electrode, Fig. 2; or, in the reflected arc heating method, we can incline two carbon or metal electrodes at an angle of about 120° and bring the material to be heated under the arc (Figs. 3 and 4) or as in the Heroult furnace operate two or three arcs in series (Fig. 5).

The advantage of heating or melting by the arc processes is simplicity and ease of manipulation. On the other hand when operating under ordinary atmospheric conditions it is difficult to avoid contamination of the material to be melted or under test by vapors from the arc.

Electric-arc Furnaces.—The electric-arc furnaces are usually subdivided into two classes, those that are designed primarily for the manufacture or refining of steel and ferroalloys and those used in non-ferrous metallurgy, or so-called electric brass furnaces. A large number of different makes of electric steel furnaces are being marketed in this country and abroad. To mention but a few of these: Heroult, Snyder, Rennerfelt, Greaves-Etchells, Groenwall-Dixon, Ludlum-Girod, Booth-Hall, Moore, Webb, Stassano, Grëne, Volta, Vom Baur and Wile.

The furnace most widely used in this country is the Heroult. It was the first arc furnace to be used commercially in the manufacture of steel. This furnace has a

[1] *Trans.* Am. Electrochem. Soc., Vol **37**, p. 665.

[2] C. S. McDowell, *Trans* A I E E Vol **34**, pp. 363-85, 1915; G. Gehlhoff, *Elektrotechn, Z.* Vol. **42**, p. 1315, 1921

[3] *Cf.* "Electric Furnaces in the Iron and Steel Industry," Rodenhauser, Schoniawa, and Vom Baur.

bowl shaped hearth, similar to an open hearth, with no electrical connections through the bottom. The electrodes pass through the roof and are suspended vertically, so as to have the arcs in series, electric current passing from one electrode to the bath and out through another electrode. Three electrodes are used for three-phase current and two electrodes for single phase current. The furnace is of rugged construction, and has a powerful and reliable tilting mechanism. The circular shape gives the maxi-

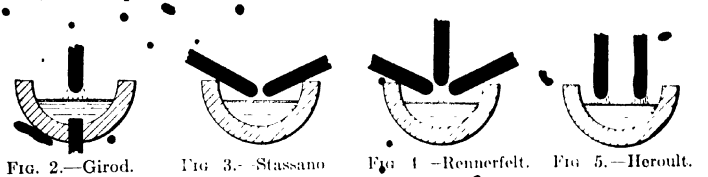


FIG. 2.—Girod. FIG. 3.—Stassano FIG. 4.—Rennerfelt. FIG. 5.—Heroult.

FIGS. 2, 3, 4, 5.—Arc-furnace types

mum mechanical strength and minimum surface for heat radiation. Reactance in the furnace and in the power circuits is reduced to a minimum, thus giving a power factor of 0.90 or higher. It is possible to do this, and still secure a minimum disturbance on the power line, due to employing low voltage and short arcs. The Heroult furnaces have been constructed in sizes ranging from 1 ton to 40 tons capacity and are operated with either basic or acid hearths. They are extensively employed in making tool steel, high-speed steel, special grade alloy steels, the melting of high-priced non-ferrous alloys, the melting of ferromanganese for addition to open-hearth steel, the making of small steel castings and malleable iron castings. The charges consist of either cold scrap or partly refined steel taken from Bessemer converters or open-hearth furnaces, or of molten iron from cupolas.

Electric Furnaces for Non-ferrous Metals and Alloys. Besides the Baily resistance-type furnace above described the Booth rotating furnace, the Detroit rocking electric furnace, the General Electric muffled-arc furnace, the Von Schlegell repelling-arc furnace, the Rennerfelt, the Northrup high-frequency furnace and the Ajax induction furnace are some of the more common installations for melting non-ferrous metals.

The Booth rotating furnace and the Detroit rocking furnace are similar in general outline: A cylindrical shell with an electrode entering from either end. The arc plays between the two electrodes and the heating of the brass or other metal bath is by radiation or indirect heating. In the repelling-arc furnace the electrodes are suspended through the top of the furnace. The electrodes are balanced so that they touch and hang together when no current is flowing. The arc is formed by the mutually repelling force when current flows in the electrodes. The extent of this action is regulated by balance weights on the electrodes.

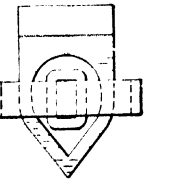


FIG. 6.—Ajax-Wyatt furnace.

In the G. E. muffled-arc furnace there are two heating units, one at each end of the furnace. Each unit consists of two vertical electrodes, a carbon wearing block for each, and two cross electrodes, which lie in a duct, one on each side of the wearing blocks. The duct is filled with granular coke or graphite which muffles the arc and supplies the heat, as numerous small contact and resistance arcs are formed in it by the passage of the current through it between the vertical electrodes and the wearing blocks, and hence to the cross electrodes. Although this furnace is inherently two-phase, it may be operated either single- or three-phase, the most satisfactory phase

voltage being from 60 to 70 volts. There is no contact between the charge and the electrodes, hence the tendency of the brass to become volatilized or pick up impurities is reduced to a minimum.

Induction Furnaces.—Electric furnaces in which the heat is generated by induction have undergone a marked development since the appearance of the Colby, Kjellin and Roechling-Rodenhauser furnaces. In steel practice the induction furnace has been largely replaced by the arc furnaces. In the brass-melting industry, however, the induction furnace is one of the most satisfactory types. The Ajax-Wyatt furnace (Fig. 6) based on patents by Hering and Wyatt consists of a vertical ring hearth. The heating is internal in the metal itself which acts as the resistor. Through the pinch effect and motor effect the brass is kept in constant circulation.

The "pinch" effect derives its name thus. When a current passes through a molten metal the accompanying electromagnetic field causes the surface layers to be

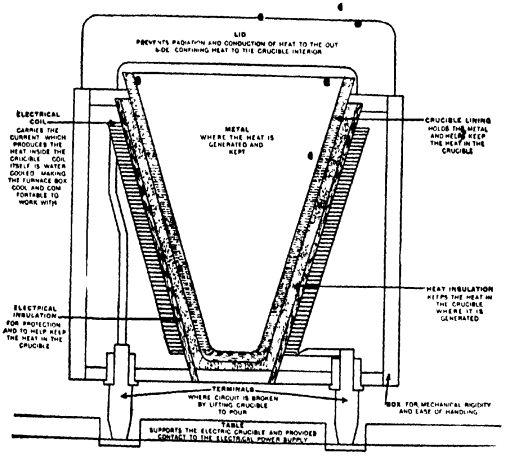


FIG. 7.—Crucible induction-furnace.

attracted to the center. This contracts the cross section, "the pinch," and if the channel be a long horizontal one the conductor is likely to be broken at some point. If the conductor be a vertical one the centripetal pressure of the outer layers cause differences in pressure that tend to drive the center of the column up and allow the outside to flow down. There is no electrode consumption and the thermal efficiency has been exceptionally high.[1] The furnace has been adopted very widely by those brass rolling mills that operate 24 hr. a day and need not often change from one alloy to another—conditions vital to the successful operation of this furnace.

The Ajax-Northrup High-frequency Induction Furnace.—Of all the electric furnaces invented and developed, this Northrup furnace is undoubtedly the most ingenious. It is in successful commercial operation at the U. S. Mint and at several silver foundries. On a small scale in laboratories some 40 Northrup furnaces have been installed. Tungsten metal can be melted in the Northrup

[1] G. H. Clamer, *Jour.* Franklin Inst., Vol. **190**, p. 473, 1920; H. W. Gillett, Electric furnaces for nonferrous alloys; *Trans.* Am. Electrochem. Soc., Vol. **39**, 1921.

furnace. The metal or alloy is heated without the use of an arc or other electrical connection. The material to be melted or treated may be surrounded completely with refractory material so that the heat losses are a minimum. A temperature of 2,600°C. can be attained within 15 min. The larger size furnaces will hold 550 lb. of pure silver operating at 75 kw., three-phase, 60 cycle, 6,600 volts. The crucible or container is surrounded by a single-layer solenoid carrying the electric current of high frequency 10,000 to 12,000 cycles per second. The coil remains cold, while the metal or alloy or other material under investigation attains a very high temperature due to eddy currents induced in it.

Unlike other induction furnaces there is no necessity for an interlinkage of a magnetic circuit with the electric circuit. The high frequency converter system has no moving parts and is highly dependable. If a non-conducting material is to be melted, a conducting crucible is used, while non-conducting crucibles are used when conductive materials are to be melted. For melting in vacuum a long quartz tube is employed. As there are no electrical connections to pass through the walls of the quartz tube, a high vacuum is easily obtained. In melting gold 180 oz. are melted per kilowatt hour.[1] Platinum melting is carried on in lime, zirconia or magnesia crucibles and since the heat is produced in the material itself, there is very little contamination. Glass may be melted in a nickel container where the temperature is not over 1,425°C.

[1] *Electrical Review*, Vol. 77, p. 184, 1920.

SECTION XV

MIXING AND KNEADING

By Dr. L. C. Reese[1]

Introduction.—Mixing and kneading are among the oldest, the most frequently employed and the most important operations in household and industry. The ancients prepared and mixed powders, lotions and ointments for medical use; they smelted metals from mixtures of ores and flux; they made and blended the beautiful colors and paints the unexcelled brilliancy and durability of which we still admire in the relics and ruins which have come down to our time, and they kneaded flour, water and leaven into dough which, baked, gave the light, spongy, wholesome and easily digested bread still forming the staple food of the civilized races.

Mixing was mostly, and kneading up to about 50 years ago was always, done by hand. The simple implements used for making the work of the hands more effective were, for small quantities, the mixing bowl or trough and stirring rod, paddle, spoon or fork, and for larger amounts, the mixing board or floor and the shovel.

Before a mixture is ready for use, it is frequently necessary that its components should be subjected to another treatment, especially to grinding and sifting; both operations, mixing on the one hand, and grinding or sifting on the other, can often be combined with the greatest advantage. This old expedient is used also with modern machinery where in any way possible and profitable. For instance, coarse materials offering the same or similar resistance to pulverizing and therefore capable of being evenly ground in the same mill, as many cereals, seeds, mineral colors, ores, drugs, dyes, chemicals, etc., are placed raw in the required proportion in the hopper of the mill, ground together, and the resulting rough mixture is then passed through one or more sifters or bolting reels, whereby usually a satisfactory product is obtained. Substances already finely powdered, as flour, ground condiments, salts, chemicals, colors, etc., were formerly mostly mixed by sifting them several times through a sieve of sufficiently fine mesh, thus removing coarse particles and loosening the materials to make them more active or more receptive to further treatment, while at the same time producing an intimate mixture. At present the mixing machine is usually preferred for this purpose, as its action is quicker and in general also more thorough; but the housewife still mixes the flour, baking powder and condiments for her cake by passing them several times through her little hand-sifter.

Oil paints, as well those for ordinary use as the finest for art paintings, were generally prepared by the painter's assistants—the color grinders—grinding and rubbing the finely powdered and sifted pigments by means of the stone into the oil spread out on the slab, until the required shade, consistency and covering capacity had been attained. This laborious and tedious work has been supplanted by the power-driven mixing machines and paint mills used in the large factories which supply the ready-made paints and colors to the trade in handy cans and to artists in neat tubes of tinfoil.

In the scientific laboratory the chemist always comminuted and mixed his substances for analysis and his chemicals to assist reaction, and the pharmacist prepared his powders, pills and ointments by means of the mortar and pestle which since the

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oldest times rightly forms the symbol of their trade. Today the chemist buys his reagents, and the pharmacist his wares from large chemical and pharmaceutical factories in which the simple mortar and pestle has long been superseded by numerous types of mixing machines. Not only in these few examples described, but in every trade in which mixing and kneading are done, production was transferred in our machine age from the craftsman, working for a limited number of his neighbors, to the large factories caring for the millions, which change was in all cases greatly assisted, and in some directly caused, by the invention of the power-driven mixing and kneading machines, following closely the development of a suitable power plant. The advantage of these modern machines does not consist so much in their better action, in the attainment of a more homogeneous mixture, but mainly in the production of much larger quantities at a huge saving of manual labor and working time.

Divisions.—Mixing operations and the appliances used are appropriately divided according to the nature of the materials to be treated into the following three classes: (1) Mixing solids with solids (coarse and powdered materials); (2) mixing liquids with liquids (also while heating, melting, evaporating, etc.); (3) mixing liquids with solids (solutions, creams, pastes, ointments, polishes, inks, concrete, etc.) To these main heads I add the following, dealing with special kinds of mixing: (4) Mixing and kneading doughs for bread (also for cake, biscuits, crackers, noodles, macaroni, etc.); (5) mixing and incorporating plastics (rubber, putty, linoleum, soap, etc.); (6) whisking and emulsifying.

In Class (1) which comprises finely pulverized substances like flour, fuller's earth, chemicals, china clay, explosives, baking powders, spice, face and tooth powders, chocolate, cocoa and other food powders, etc., as well as materials of a larger size and coarser shape, as minerals, drugs, tea, coffee, insulating materials, fertilizers, glass mixes, graphites, etc., all the more generally used mixing contrivances, mixing machines with their various stirrers, agitators and blades, mixing drums and tumblers, etc., are employed to intermingle the ingredients of a mixture so intimately as to form a completely uniform, homogeneous mass. I therefore first describe these general devices, and then particular machines and apparatus adapted and constructed for working special materials.

Basic Principles.—When the quantity of matter to be mixed in one batch by means of a machine provided with a certain mixing device is increased, the size of the container of the machine must, of course, be increased in accordance with the increased bulk of the mass to be worked, and in three dimensions, but the active surface of the mixing device while retaining the same principle of construction can only be enlarged in two dimensions. It naturally follows that the amount of power and time required to obtain the same result for a unit of mixture does not remain the same for all sizes of the same construction, but increases at a considerably quicker rate than does the number of units for which the machine is intended. In general, the highest degree of homogeneous mixing can be attained in a machine only up to a certain size; above that the result deteriorates more and more.

When having to mix very large quantities of materials at the same time, it is therefore more advantageous to employ a battery of smaller machines, which do the work in the most effective and economic manner, than to try to construct for the purpose over-large machines which can only give imperfect results. For the same reasons, when trying out new mixing devices, we often find that they seem to show very promising improvement in the experimental stage, but disappoint when the machine is constructed on a commercial scale.

In order to produce in a machine several mixtures of exactly the same composition and degree, it is necessary accurately to weigh or measure the materials to be mixed, and to treat them in exactly the same manner, especially for the same number of revolutions of the agitator and for the same length of time. Mixing operations are greatly facilitated and accelerated by charging the ingredients into the machine gradually, and as far as possible in the same proportion in which they are to form the required mixture. Continuously working mixing machines provided with separate hoppers for each ingredient, delivering them in the right proportion into the machine without interruption, and with an outlet through which the mixed mass is discharged in a continuous stream, have been frequently constructed and tried, but in these machines neither the feeding nor the mixing has hitherto been of that uniformity which in general the accurate work of mixing and kneading requires; they can therefore be used only in exceptional cases where absolute accuracy and homogeneity are not required.

In many mixing operations, for instance in the manufacture of chemicals, pharmaceutical preparations such as pills, drops, tablets, etc., of explosives, of dry colors, color pastes, artists' oil paints, etc., it is imperative that the mixing be so thorough and continued for such a time that the ingredients form a completely homogeneous mass, otherwise the chemical and pharmaceutical products would have unequal and undesired effects, the explosives give uneven discharges, the colors and paints show streaks and spots, etc. In these cases it is therefore necessary accurately to determine the end of the mixing operation.

The finished mixture has usually a characteristic appearance, color, consistency, density, etc., by means of which after some experience the eye or hand can readily recognize at any time during the mixing operation the state of the mass under treatment and its completion. When the ingredients consist of powders of different colors, tints or shades, a small sample is thinly and evenly spread by means of a small spatula on very smooth white paper; the number of the various colored streaks and spots thus exposed and their different shades indicate the degree of mixing, which is finished when the whole shows a completely even color. When the substances to be mixed are composed of fine particles having a different shape, often also a slightly different size and color characteristic to each ingredient, the homogeneity or intimateness of the mixture produced can be judged with fair accuracy by examining a sample under a magnifying glass or microscope. In many cases also a suitable chemical test can be devised to find the end-point of the mixing operation.

The value of a mixing machine does not depend solely on the efficiency, duration and cost of the work it performs, but is influenced by the ease and quickness with which it can be charged, discharged and cleaned, its bearings oiled, its driving gear started and stopped, etc. The protection of the attendant from being caught by the moving parts inside and outside the machine, as blades, pulleys, gear wheels, belts, etc., is also an important consideration when choosing the general arrangement and position of the machine.

All mixing and kneading machines—including those intended for comparatively light work—should be strongly built and rigidly fixed to their frame and supports so that all vibrations which might damage the machine or its driving gear or diminish the efficiency of its working are prevented. The bearings of the running parts of the machine must be so arranged and protected that no lubricating oils or other materials used therein can enter into or come into contact with and thus contaminate the contents of the mixer, and that no particles of the mixture can penetrate into and thus gradually destroy the bearings.

Mixing machines are usually made of iron and steel. In cases where iron must not rub against iron, the mixing parts are made of brass, bronze, wood or the like. When materials are to be mixed that for chemical reasons must not come into contact

with iron, the interior of the machine including the mixing devices may be tinned, lined with lead, silver, nickel or other metal, enameled or protected in some other suitable way.

For heating or cooling materials while being mixed, the trough or tank of the machine in which they are treated is surrounded with a jacket through which a current of steam or of cooling water is passed; also hollow mixing blades and agitators have been constructed for increasing the effect of the jacket. In order to prevent the particles of the mixture from caking on or adhering to the heated or cooled walls of the vessel, which would make their proper mixing impossible and at the same time greatly diminish the effect of the jacket, suitable scrapers arranged at or forming one piece with the mixing device and passing closely along the walls must be employed to keep them clean and thus distribute the heat evenly in the mass.

Provided the duration of the mixing operation is in all cases the same, in general each type of mixing device requires a different speed for producing from the same materials the same kind of mixture, and every mixture composed of different ingredients or of the same ingredients in different proportions, when treated in the same mixer, makes a different speed necessary for obtaining the same degree of intimateness. Therefore, in order to mix successfully, attention must be given that the driving gear always provides the correct speed, and the operation is continued for the proper time, as determined for the mixture by experiment and experience.

The higher the speed, the greater is the amount of power required as well as the wear and tear of the machine. In some cases it has been found advantageous to change the speed of the mixing device during the operation, for which a change-speed gearing, like Reeves', allowing one to alter the speed at will within certain limits, is usually employed. Machines, in which it is desired to make several mixtures requiring different speeds, are generally provided with interchangeable gearings, one for each speed needed. To reverse the direction in which the agitators or blades rotate is a means frequently used to accelerate the mixing operation, and to facilitate the removal of the finished mixture from the machine. A convenient reversing device is the well-known double-clutch, slide-mounted on the driving shaft of the machine between two loose power pulleys or gear wheels capable of rotating the shaft in opposite directions.

Hoppers suitably constructed with inclined sides and arranged above the machine are generally employed to charge it with solid materials; the outlet opening of these hoppers is frequently provided with sliding shutters or similar means to cause the substances to be mixed to enter the machine gradually and in an even stream. For charging liquids into the mixer usually a feeding tank is placed above it; the outlet pipe is fixed to its bottom or lower part and provided with a stopcock for regulating the flow of the liquid therefrom; a gage glass serves for observing and measuring the quantity of liquid contained in and leaving the tank.

A great assistance in accurately charging a mixing machine and a considerable saving of labor and supervision are gained by employing automatic weighing hoppers and tanks, in which these containers are attached to scales provided with automatic means to shut off the current of material entering them as soon as the weight of the mass contained therein is equal to that required and previously adjusted on the scale beam. Mixing and kneading machines are generally emptied by turning the mouth or charging opening of their receptacle downward; only in the rare cases where this is impossible they are discharged from the top or through doors or manholes arranged at their bottom or sides. When the center of gravity of those parts of the machine to be revolved and of the mixture contained therein lies in or near the axis round which the former can be turned, little power is required for this purpose, so that it can be tipped over by hand; but where this is not the case, suitable power gearing of ample strength or the assistance of a counter-weight mechanism must be employed.

When great accuracy is desired, modern machines are equipped with revolution counters combined with an adjustable device for automatically stopping the machine as soon as it has made the number of revolutions for which the device has been set.

The most favorable construction and size of a mixing machine for a given quantity and proportion of its ingredients, the most advantageous duration of the operation, and the exact velocity of the rotating mixing devices for obtaining the best possible result can only be ascertained for each case preliminarily by experiment and definitely by experience. The movements of the particles and molecules of a mass being mixed are—even when a simple device is used—too complicated for any mathematical calculations which might serve as a basis for the construction of a mixing machine; they have been attempted, but led only to disappointment. A thorough knowledge of the effect of the simple standard mixing devices alone and in combination and of the properties of the substances to be mixed and of the mixture obtained therefrom, and carefully planned and executed experiments form the sound foundation on which a designer must base the construction and arrangement of successful mixing and kneading machines.

Mixing Solids with Solids.—The facility with which solid substances can be mixed depends on their physical and chemical qualities: if their particles are coarse or fine, long and thin, or short and plump, round or angular-shaped; if they are absolutely free from moisture or air dry or contain still a certain amount of water; if they are hygroscopic or not; if their particles adhere to each other readily, hardly or not at all; if their qualities are altered by a slight change of their temperature, and if they chemically affect each other.

When solid substances having a different specific gravity are violently shaken and stirred in a receptacle, the heavier ones will collect in the bottom and the lighter ones in the top layers of the mass. If substances thus treated have about the same specific gravity, but are different in size, the coarser particles will gather in the top and the finer ones on the bottom, and if their particles are of different shape, partly spherical, globular or plump and partly angular, polygonal or elongated, the first—the round ones—will collect in the lower part, and the second—the cornered ones,—in the upper part of the mass. For these reasons the mixing appliances for such matters must be so constructed that the lower layers of the mixture are turned again and again on top of the upper layers, and so gently that no reshifting or rearrangement can take place, other than the one designed.

In order to make a mixture of different solid matters as nomogeneous as possible it is necessary to isolate all the single particles of the components from each other to combine them again in a fresh order and to repeat these operations until the particles are distributed through the whole mass in as even and regular a manner as required. For this purpose, the single particles are tumbled over each other, pressed down between each other and thrown in crosswise and opposite sidewise directions by rotating either the receptacle containing the mass to be mixed, or by rotating an agitator stirrer, mixing blade or the like arranged in a stationary receptacle for the mass to be treated, or both the receptacle and the stirrer. The velocity of the rotation must be such that the centrifugal force cannot appreciably influence the mixing operation and its result. A temporary reversing of the direction of the rotation during the operation is sometimes of advantage.

The receptacle, by the rotation of which the mixture is to be produced, is usually circular in cross section, consisting of a cylinder, drum or cask. If an agitator forms the exclusive expedient for mixing, it is in general placed within a stationary trough having a half cylindrical bottom and revolves in an axis identical with that of the latter, the outer tips of the agitator passing along the inner surface of the same. The

square open upper part of the trough is usually formed as a hopper and serves for charging and discharging the machine. In case two or more blades are used for a common receptacle, the latter consists of two or more adjacent parallel half cylinders.

The amount of power required for mixing solid materials is comparatively small.

Mixing machines, in the narrower meaning of the designation, are apparatus in which the materials to be treated are placed in a trough or tank and mixed by a mechanism revolving therein. For solid substances usually a half cylindrical trough is used, the sides of which are extended upward to a square hopper. The materials are mixed by an agitator or mixing blades supported in stuffing boxes fixed to the flat sides of the trough in such a manner that their axis of rotation is identical with the axis of the trough cylinder.

The machine is charged with the material while the trough with its hopper is upright, and discharged by tilting it over so that the finished mixture drops from the cylindrical bottom part along the sides of the hopper into the receptacle placed underneath. This easy and quick method of filling and emptying the mixing trough is a great advantage and the reason for the nearly universal employment of this construction. The bearings, in which rotate the ends of the agitator shaft protruding from the trough, must be durable and tight so that no fine particles of the materials being mixed can escape from and no extraneous matter, as lubricating grease or dirt, can penetrate into the interior of the trough. Dents, pockets, corners, angles, cuts, incisions, grooves and the like, in which particles of the substances to be mixed might settle and be retained, thus escaping the treatment, must be avoided as well in the cylinder or trough, as in the agitators or blades. The shape and surface of the rotating devices used must be such that, while they pass through the mass being mixed, all the particles of the latter are successively acted upon by direct touch and then easily slip or drop away again into the intermingling mass. The mixing trough and agitator are in general made of a suitable metal, usually iron which, if required, is tinned, nickel-plated or enameled. In case rough materials, the particles of which are so sharp and hard that they wear away the metal, are to be mixed, it is a good plan to provide the interior of the trough with a replaceable lining of steel-plate. In order to prevent dust arising during the mixing operation from entering the surrounding atmosphere, the open top of the trough hopper should be provided with a well-fitting lid.

Samples of the mass under treatment should be taken only after the machine has been stopped. The eagerness of the attendant is often so great that he tries to test or take a sample from the mass being mixed without interrupting the work of the machine. This thoughtless want of precaution has led to frequent accidents. The machine ought therefore to be arranged in such a manner and put into such a position that the attendant cannot reach into it during the operation; and, where this arrangement is not possible, a lid ought to be provided which cannot be opened while the agitators are rotating. In some states the rules of safety prescribed by law require well-locking safety lids for all mixing machines.

The agitators are usually belt-driven, in the simpler machines the driving pulley being fixed directly to the part of the agitator shaft extending outside the trough; in more complicated machines, where two or more agitators are revolved by means of gearwheels meshing with each other, the driving pulley is mounted on a main shaft arranged in the framework supporting the machine; a pinion fixed to this shaft and meshing with the gearing of the agitators imparts then the motion to the latter. Lately by reason of its convenience and lack of parts requiring frequent repairs like belts which only too often need to be taken up or mended, the direct electric drive of mixing machines by means of gearwheels has been generally introduced in factories where this power is available at a reasonable price.

The speed of the agitators is usually expressed, as for all rotating devices, in revolutions per minute. When the diameter of an agitator is increased, the circular path which the lengthened part describes will be longer than that traversed by the original part; the effect of the former on the materials to be mixed will therefore be greater than that of the latter; in order to equalize these conditions, it is necessary to decrease the number of revolutions according to the increased diameter with due consideration of the particular shape of the agitating device and of the nature of the materials under treatment.

When the machine is charged when the agitator is at rest, the latter has at first to overcome the resistance of the inert mass to be mixed, which requires a considerable greater amount of power than is necessary during the operation itself when all the particles are in lively motion. This excess of power required depends on the nature of the materials to be mixed, the width of the mixing trough, the height to which it has been filled, and the shape of the agitator, and must be taken into consideration when installing the driving gear of the machine. In order to avoid the sudden jerk when starting a fully charged machine, most attendants prefer to have the agitators running before introducing the materials into the mixing trough.

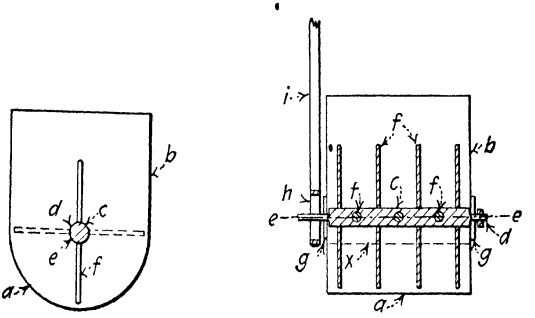
I have often been asked what I consider to be the most advantageous dimensions of the trough of a mixing machine for solids in regard to its length and diameter, if an absolutely homogeneous mixture is to be obtained. The area affected by any point of an agitator at any moment under the most favorable circumstances cannot exceed a right triangle the base of which is the axis of the agitator and the sides of which form an angle of 45° with the vertical line drawn from the given point to the axis of the agitator. If therefore that part of an agitator working in the middle between the flat sides of the trough is to have any influence at all on the particles situated at these sides, it is necessary that the length does not exceed the diameter of the trough. This deduction is in complete conformity with experience and experiment. In cases where the agitator consists of arms passing closely along the vertical ends of the trough and so constructed as to drive the particles of the mixture from the sides towards the inner part, the thickness of these arms, measured on a line parallel to the axis of the trough, may be added to its diameter for its total length. The troughs of the now usually employed various types of mixing machines, in which the mixtures are made batch-wise, agree completely or very nearly with the condition laid down above; only for machines in which agitators are used causing a predominating sidewise movement of the mass under treatment, and which are usually intended for continuous work, troughs of greater length have been tried. I describe in the following paragraphs, first, the less elaborate forms of the agitators used in this kind of machines and their effect, illustrating these devices by means of the diagrammatic Figs. 1 to 9 in all of which *a* represents the lower, half-cylindrical part of the trough containing the materials to be mixed, *b* the open hopper above *a*, *c* the agitator, *d* the agitator shaft and *e* the axis round which the shaft *d* and the agitator *c* rotate, and which is identical with the axis of the cylindrical part *a*.

When first constructing machines to perform the work done by their hands and arms, men always try to imitate their shape and action. Thus we perceive in the earlier mixing machine stirring rods, fixed to the revolving agitator shaft, replacing the action of the human fingers. Figures 1 and 2 represent vertical sections of the mixing trough and agitators of this simple machine, Fig. 1 in a plane vertical to the axis *e*, and Fig. 2 in a plane through the length of the latter. The round or square rods *f* are fixed to the shaft *c* which is supported by the bearings *g* arranged in the sides of the trough *a*, and rotated by means of the pulley *h* and belt *i*. The rods *f* which may be of any convenient number, are arranged in alternate rows and so long that they pass along the circular bottom of the trough *a* which is as long as its diameter; their length was usually 9 to 15 in.

In this and similar machines in which the shaft extends their whole length, it is usually enlarged to a hub into which the rods or other mixing devices are screwed or fixed in any other suitable way, or with which they are cast in one piece.

When this type of machine is charged above its shaft or hub, it does not mix well, because the particles surrounding the latter are hardly affected even when the agitator is rotated quickly; the trough ought therefore only to be filled up to a line fairly underneath the shaft, as indicated in Fig. 2 by the dotted line X. When the agitator c is thus rotated slowly—say 8 to 10 r.p.m. the rods f pass through the mass in the trough a doing little more than disturbing it; no real mixing can take place, but, when the speed is increased to 30 to 60 r.p.m., in accordance with the material under treatment, the whole mass will be whipped into motion, the particles whirling in different directions and at different speeds through, between and against each other, whereby a thorough mixing is made possible.

When the substances to be mixed are partly coarse and partly fine, or of different size, the mixing will remain rough, as the rods will always rake the coarser particles upwards into the top layers again. In case all the ingredients are of powder form, but



FIGS. 1–2.—Stirring-rod mixer.

differ greatly in regard to their specific gravity, the heavier ones are inclined to collect mainly at and near the walls of the trough a, and their mixture will thus not be perfect. But when the powdery substances have the same or nearly the same specific gravity, they intermingle in this manner well, and the mixture will be practically homogeneous after the operation has lasted its due time. This simple machine which requires only a very small amount of power was formerly frequently used for mixing paints, different kinds of flour, powders etc., but is today mostly replaced by more modern devices.

In order to accelerate and intensify the mixing, two or more rod agitators were sometimes arranged in one trough for combined work, the rods of the one agitator passing through between those of the next agitator with their tips near to their respective hubs. Figure 3 represents a machine which I saw a good many years ago in an ocher mill where it was successfully used for blending ochers, umbers and similar pigments to a completely uniform mass of exactly the same even color. The three agitators c, c_1 and c_2, were inclosed in the polygonal wooden box a serving as mixing trough; their parallel shafts were placed at distances from each other somewhat greater than the length of their rods. The driving gear was so arranged that, when the agitator c_1, rotated in one direction, c_2 revolved in the same and c in the opposite direction. The rods f, f_1 and f_2 were simply securely screwed into wooden hubs in rows of four, in planes vertical to the axes, and f and f_2 situated between the planes of two adjacent rows f_1. The box a was changed through the door k at its top nearly up to the hub of the agitator c_1, as indicated by the line X, and discharged through the door

l at its bottom; both doors were tightly locked during the operation. The capacity of the machine was 5 to 6 cwt., and the average time of mixing for obtaining an absolutely blended color 4 to 5 min.

The general arrangement of the machine shown in Fig. 4 is the same as that of Fig. 1 with the exception that the rods *f* are replaced by paddles *m* and m_1, the broad, straight outer edges of which pass closely to the inner surface of the trough *a*. The width of the broad upper part of the paddles is somewhat greater than the distance of their centers so that their alternately arranged rows *m* and m_1, cover more than twice the whole length of the mixing trough *a* when the agitator *c* is rotated. The power required for the same speed is naturally greater in the paddle- than in the previously described rod-agitator. At a speed of about 10–20 r.p.m. the paddles *m*, and m_1 will press the layers of materials at the bottom of the trough *a* forward and upward along its cylindrical wall, the portion retained, when above the mass, dropping on to the top of the latter, while the rest escapes through the open space between adjacent paddles and at their back edges into the upper layers; the empty spaces produced behind the moving paddles are at once filled out sidewise and from the inner and upper layers; in this way all the ingredients are gradually and gently intermingled, even when the difference in their specific gravity is considerable

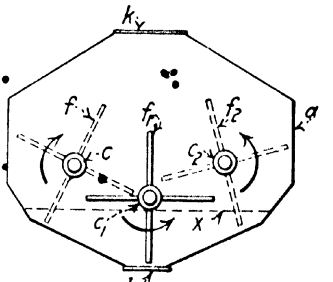
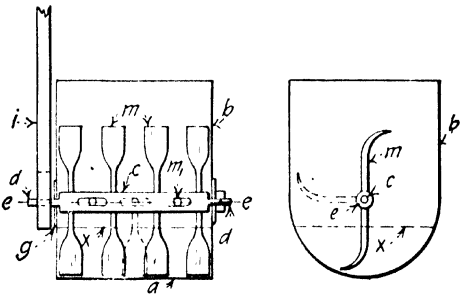


Fig. 3 Pigment mixer.

The device works well for finely pulverized substances and for coarser ones of small

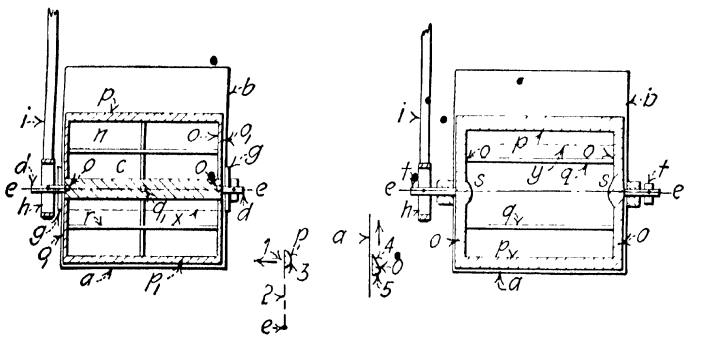


Figs 4 5 Paddle mixer.

and practically equal size, but larger sized and fine materials can not be thoroughly mixed together by flat paddles, as during their upward movement they will retain the coarser particles, while the finer ones escape through the interstices of the latter and are thus sifted out. In this case the paddles are constructed in the shape of scoops or shovels, in the concavity of which, pointing in the direction of the rotation, the finest particles will remain, until at the highest point they are ejected onto the top of the mixing mass. Sometimes it is of advantage to arrange the scoops or shovels *m* and m_1 pointing forward as illustrated in Fig. 5, their broad front edges acting as scrapers and catching up everything in their way. Considering the construction, the mixing effect is good and at all events satisfactory for the purposes for which this kind

of agitator is frequently used, as mixing of different minerals, cereals, chemicals, lumps of color, clay, etc., ores with flux, glass mixes, etc., etc. The result is also here more satisfactory, when the top of the mass to be mixed is kept somewhat underneath the hub of the agitator c, as shown by line X in Figs. 4 and 5; a higher speed of the agitator—say 30 to 40 r.p.m. is of little or no advantage in this type of machine.

In order to counteract the friction of the particles of the mass under treatment on the vertical sidewalls of the trough, the machine shown in Fig. 6 is provided with crosswise arranged side scrapers o and o_1, which at the same time serve as main support for the four narrow blades p, p_1, which extend the whole length of the trough a. The scrapers o and o_1 are fixed to the hub c and arranged so that their sharp front ends are drawn tightly along the surface of the side walls during the rotation of c; the blades



FIGS. 6–9. — Mixers with scrapers

are riveted or otherwise rigidly fixed to the outer ends of the scrapers in such a manner that their outer edges pass closely to the circular surface of the trough bottom a. The crosspieces q and q_1 connecting the blades p and p_1 with the hub, and the crossrods r connecting two opposite scrapers are intended to strengthen the rigidity and increase the effectiveness of the device.

The agitator shown in Fig. 7 has only two blades; its side scrapers o are reinforced to arm-like structures and cast in one piece with the broader and strengthened blades p and the bosses s with the trunnions t which replace the ends of the agitator shaft d in the devices described above. In this way the obstruction of the shaft and hub to the mixing operation is avoided, and the trough may be charged up to the line y. Often crossrods q connecting the arms o and similar, even more complicated contrivances are used with the intention to improve the mixing effect of the arm-blade agitator. Of great importance to the good working of the latter are the shapes of the front and back surfaces which are in active touch with the mass in the trough. Figure 8 is a cross-section of the blade p in a plane vertical on the axis e of the device, and Fig. 9 a cross-section of the side arms o in a plane parallel to the axis e. In Fig. 8, (1) indicates the front surface of the blade acting on the material and situated in its whole length in the plane (2) passing through the axis e; the back surface (3) of p is curved so that the particles coming into contact with it easily slip and drop away again.

In Fig. 9, a denotes a sidewall of the trough of the machine, and o the sidearm moving closely along a; the front surface 4 of o is inclined in the direction of the rotation indicated by the arrow, the particles at and near the wall a being thus forced away from the same into the interior of the mass; the back surface 5 of o is curved so that particles gathering in the angle formed by it and the sidewall a are not retained there, but drop easily away during the upward movement of the arm o. At a slow

speed—say 10–25 r.p.m.—powdery substances and coarse ones of moderate size are well mixed in this type of machine; the amount of power required is not greater than that necessary for the same work in the machine shown in Fig. 4.

The simple arm-blade agitator just described is frequently used in a modified construction for mixing liquids, doughs and pastelike masses; but though sometimes useful for mixing solids, it has been in most cases superseded by its combination with the oblique-disc agitator and double-trough device and their numerous modifications and imitations. This particular construction was introduced about 40 years ago; in the belief that a good mixer is necessarily also a good kneader for bread dough,[1] the machine was at first especially intended for this heavy work and therefore was built very strongly and solidly which is a great advantage for any mixing machine.

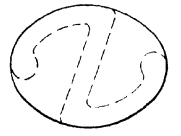


FIG. 13

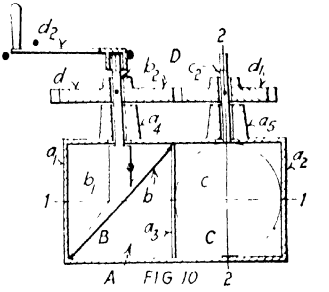


FIG 10

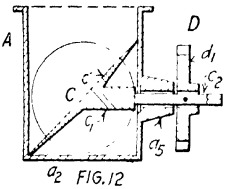


FIG. 12

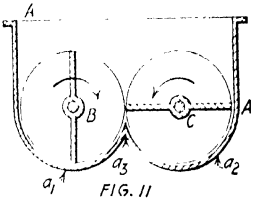


FIG. 11

FIGS 10 13.—Oblique mixing-disc machine.

The excellent result of the mixing, the short time and small amount of power required together with the simplicity, durability and practical freedom from the frequent repairs which are such a drawback in many other constructions and lighter built machines, are the reasons that this particular machine is now employed in practically every trade in which mixing is done, and in every civilized country. Figures 10 to 17 show the principles of the construction of the double-trough and oblique disc-mixing machine and are based on the patent drawings[2] describing the original ideas of the inventors. Fig. 10 is a horizontal section of the machine through the axis of its agitator, Fig. 11 a vertical section on the line (1 1) and Fig. 12 on the line (2 2) of Fig. 10; Fig. 13 shows the elliptical circumference of the agitator blades. A indicates the mixing trough, B and C the two agitators and D their driving gear; a is the upper hopper-like part of the trough A; a_1 and a_2 are the two equal parallel half cylinders forming its bottom; a_3 is the edge or saddle in which a_1 and a_2 meet, and a_4 and a_5

[1] See p. 556.

[2] U. S. Pat. No. 180,568, Aug. 1, 1876, PAUL FREYBURGER for "Kneading Machine," U. S. Pat. No. 254,042, Feb. 21, 1882, PAUL PFLEIDERER for "Mixing and Kneading Machine," U. S. Pat. No. 34,968, Feb. 26, 1895, PAUL PFLEIDERER for "Machine for Mixing, Kneading, etc."

are the stuffing boxes in which the shafts of the agitators B and C rotate coaxially to a_1 and a_2 which must be so arranged to each other and in regard to the saddle a_3 that the tips of the agitators B and C, when rotating, pass as closely as possible to each other above a_3 in the center part of the trough A. b indicates the elliptical disc forming the mixing blade of the agitator B, b_1 its hub or stem.

The ellipse forming the circumference of the blades, Fig. 13, has as its minor axis the diameter of the cylindrical part of the mixing trough, and as its major axis the hypotenuse of a right-angled triangle the two sides of which are respectively equal to the diameter and the length of the trough cylinder. The plane bounded by this ellipse, which we may consider as the ideal working surface of the design, forms the front of the blades b and c the centers of which are identical with the centers of the trough cylinders a_1 and a_2; b and c are arranged at their corresponding hubs b_1 and c_1 and in regard to the shafts b_2 and c_2 revolving coaxially to a_1 and a_2 respectively, in such an inclined position that the tip ends of the major axis of the ellipse, describe when rotated circles closely identical with the circles forming the circumference of the two opposite flat ends of the cylindrical parts of the mixing trough a_1 and a_2, as shown in Fig. 11. In Fig. 10 the minor axis of the ellipse of the blade b is vertical to the plane forming the open top of the half cylindrical bottom a_1, while that of c lies in the corresponding plane of a_2, appearing, seen from above, as a circle; in Fig. 12 c is in the same position, but seen from the side. When the blades are revolved as indicated by the arrows in Fig. 11, they act on the material to be mixed twice, first with their front and then with their back surface, during each rotation. In order to give to the blades the necessary strength, their back surfaces decline towards their hubs as shown in Figs. 10 and 12 and can therefore not be so effective as the even front surfaces, the hubs naturally also obstructing the mixing at this side of the blades. Like the edges of the two blades of the agitator shown in Fig. 7, those of the elliptical blade describe in outline a cylinder corresponding to the half-cylinder of which the bottom of the trough consists, but act in consequence of their greater length on a correspondingly greater amount of particles. The elliptical blade not only pushes the material forward, then upward, and turns it over, but causes two strong sidewise motions during each revolution, first to the one and then to the opposite end of the trough.

This strong effect is still greatly enhanced by the use of two such blades B and C rotating in the double trough A in the direction shown by the arrows in Fig. 11. At each revolution each blade will twice press over a portion of the material contained in the half cylinder, in which it moves, into the adjacent one, and will twice draw portions from the latter into its own half, provided—of course—that the trough is charged with material well above the saddle between its two half-cylindrical bottom parts. A different velocity of the two blades which prevents them from working against and thus obstructing each other, has proved advantageous. In Fig. 10 the proportion of the size of the spurwheel d to that of d_1 is 4 : 3; the refore the blade C driven by d_1 will make 4 revolutions in the same time in which the blade B rotated by d makes 3.

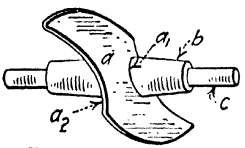


FIG. 14.—Cut-out blade for dough.

It is obvious that a full size oval blade arranged and worked as described will exercise a considerable outward pressure on the material being mixed; and, when the latter is of a thick and heavy character or plastic like dough the particles of which adhere strongly to each other, the strain on the machine and the power required to drive it will be especially great. In order to avoid these strains and to facilitate the working, gaps having usually curved outlines were provided in opposite sides of the periphery of the disc blade, as shown in Fig. 14.

The construction of the agitator shown in Fig. 10, in which the shaft carrying the

disc blade is supported only at one end of the trough, is in most cases too weak for work on any large scale. In commercial machines therefore the shaft revolves usually in bearings provided in each end of the machine and, when extending the whole length of the trough, is reinforced to a hub at the middle part of which the oblique blade is arranged; the latter, the hub and the shaft are usually cast in one piece. As this long shaft or hub takes up a not inconsiderable portion of the active capacity of the mixing trough without assisting—if not actually obstructing—the mixing operation, it is omitted where the shape of the blade required for the material to be treated, allows to do so, and the blade is in that case fixed, as shown in Fig. 15 at the ends of its major axis to sidearms constructed like those described in Figs. 7 and 9.

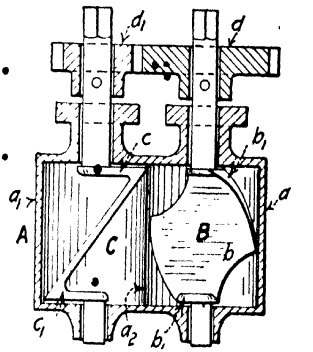
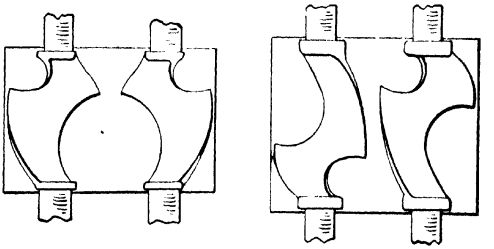


Fig. 15.—Dough mixer.

In Fig. 14, a indicates the blade, b the hub and c the shaft of the agitator; a_1 and a_2 are the gaps cut from the ideal elliptical plane of a. In Fig. 15 a and a_1 denote the two half-cylindrical bottom parts of the mixing trough A with a_2 the saddle or cutting edge between them; B is one oblique blade and b_1 the sidearms carrying it, while c and c_1 indicate the corresponding parts for the blade C; d is one spurwheel, and d_1 the other; the proportion of the diameter of d to that of d_1 is 7:4. It will be noted that, when looking at the agitator in the direction of the minor axis of its blade, as at C, the blade C forms with the sidearms c_1 and the hubs the letter Z.

In the actual blades the gaps in the perimeter of the disc plane are constructed according to the effect to be obtained, small or large, and either of the same or similar


Figs. 16 17. Cut-out blades.

size and shape as in Figs. 14 and 15, or of unequal and unsymmetrical dimensions as in Figs. 16 and 17. In Fig. 16 the smaller gaps of the two blades are arranged at one end and the larger ones at the opposite end of the double trough, while in Fig. 17 a small gap of the one blade is shown opposite to the large gap of the second blade at each end of the trough. I consider the last arrangement preferable in all ordinary cases of mixing and kneading. In some cases only a comparatively narrow strip is left at opposite sides of the circumference of the blade besides the small middle part connecting the two outer sections, as shown in dotted lines in Fig. 13. As the iron or other material of which the blade is made must—of course—be of a sufficient strength and thickness for the work, and as the active surfaces lie in one plane, but at opposite,

sides of the blade, the latter will have a peculiar twisted shape and appearance. A completely correct pattern for a blade of this class is obviously very difficult to make; expediency in pattern-shop and foundry are probably the reasons that blades made in later years often deviate to their detriment from the fine, correct forms produced by the original makers. Angles and corners not quite avoidable in this construction must be made as obtuse as possible or rounded off, as also all back surfaces curved, as already explained in regard to Fig. 7. All parts of the blade and especially the corners must have as smooth a surface as possible in order to get the best result.

A reversing of the direction of the rotating blade will quickly remove particles from corners where they are not under the full mixing action, and thus greatly assist in the mixing operation, especially when sticky, adhesive or plastic masses are treated. When the direction of the two blades in a double trough is reversed, the material will be drawn away from the middle part of the trough and pressed against and piled up the sides of the trough and its prolongation, and will thus greatly facilitate the passage of the finished mixture from the machine when the latter is tilted.

The strong side currents prevailing in the material treated in this class of mixers make it possible, without appreciably impairing the effect, to lengthen the half-cylindrical trough somewhat above the proportion to its width given above, page 535. The ideal proportion of the length to the diameter of the trough for a single blade machine would be 1:1, and it should in practice not be increased above 3:2. The proportion 1:1 is shown in Fig. 10, for a two-blade machine, the length of the double trough *A* being equal to the diameter of one half-cylinder, thus half of its total width. The same proportion, but modified by the deduction of the combined widths of the two sidearms, is given in the Figs. 15 and 16. When applying the above limit, 3:2, of the one-blade to the two-blade machine, the proportion for its trough would be 3:4; but, as this machine is more effective, the proportion may be still slightly increased; for larger machines the trough is usually made about square, 1:1, and in some cases even a shade longer than wide. It appears obvious that with the increase of the length of the blade its mixing effect will be diminished and the time required for the mixing prolonged.

The speed necessary for the elliptical agitator, when mixing solids, is a low one, 9–25 r.p.m., and the power consumed is small indeed. In a two-blade machine the relation of the speed of one blade to that of the other one is arranged with advantage, according to the materials to be mixed, between 2:3 and 1:2. For instance, I mixed in a two-blade mixer 420 lb. of flour with 8 oz. tartaric acid, the speed of the one blade being 8, and that of the other one 13 r.p.m., and obtained after 11 min. a mixture which according to a number of chemical tests of the different portions of the mass was completely homogeneous. The two-blade machine still mixes perfectly well when charged to the top of the blades, which should just protrude from the mass when at rest; this—in comparison to other types of mixers—extraordinarily large working capacity of the trough in proportion to its size is one of the greatest advantages of this machine

Figure 18 represents the usual form of a single-blade mixer, the trough being tilted for emptying, which is effected by means of a wormwheel and quadrant worked by a handwheel. It mixes substances offering a slight resistance as light, dry powders, thin pastes and doughs very well.

Figure 19 shows the best-known type of a two-blade mixer, the trough *a* being completely tilted, thus showing the Z-shaped blades *b* and *c*. The trough is counter-balanced, *d* designating the rod and chains carrying the counter weight and *e* the hand-driven gearing working the arrangement; *f* shows the reversing gear. This machine is highly efficient in every kind of the ordinary mixing of solids, doughs, pastes, etc.; it has the largest capacity possible for this type and is easily emptied and cleaned; it is a good all-round mixer.

In Fig. 20 the wing-like blades of reduced elliptical shape are made of one piece with the hub and shaft. This form mixes heavy powdery substances, the specific gravities of which often greatly differ, very satisfactorily. Figure 21 shows in a nearly square double-trough two agitators each of which carries two parallel winglike

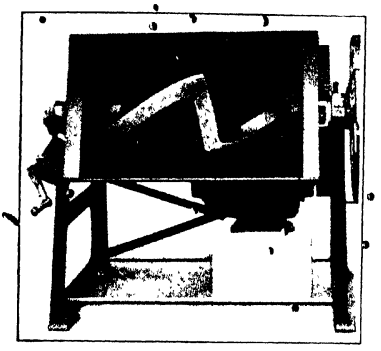


FIG. 18.- Single-blade mixer

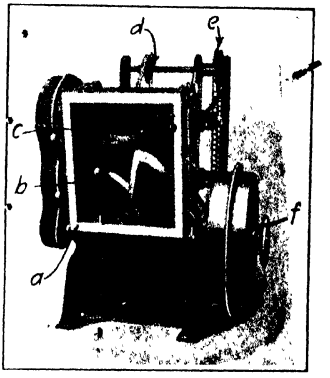
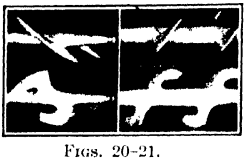


FIG. 19.- Two-blade mixer.

blades arranged obliquely at the hub in such a manner that the inner tips of these blades rotate in a circle close to the inner surface of their half-cylindrical trough part and in the middle of its length. It is used for very heavy work. Other characteristic blades of this kind are mentioned in later paragraphs.

Figures 1 to 17 describe only the simple, fundamental shapes and arrangements of mixing blades; extraordinarily numerous are their modifications, additions and combinations designed either for a certain purpose, a particular kind of mixing or particular materials to be mixed, or for general improvement of the mixing effect. These improvements consist mostly in turnings, curvatures and inclinations of the active



FIGS. 20-21.

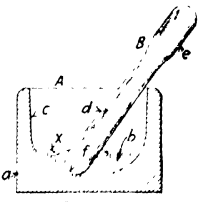


FIG. 22.

planes of the blades, in bendings and angles in the sidearms and cross connections, in specially shaped and arranged paddles and rods, in little plates, plain as well as of an intricate shape, fixed to the shaft or hub, the main parts of the blades or its sidearms, and in wire-like rods crossing in any direction from one part of the blade to the other one or spreading from one set of arms to the following ones. It would be of no advantage to describe all these more or less complicated minor devices; though sometimes answering their special purposes well enough, it is only too often that on exactly testing them, the unbiased experimenter finds that if there is any improvement in the mixing effect perceptible at all, it is infinitesimal, as the additional currents and

movements caused by the modifications interfere with, derange, counteract or deflect the main and decisive currents produced by the original blades, thus weakening and diminishing their force and effect, while at the same time requiring a greater amount of driving power.

The mortar and pestle—already mentioned—are made of steel, brass, china, clay, glass or agate according to the substances to be treated. Figure 22 represents a vertical cross-section of a mortar A and its pestle B. A consists of the walls a, of the mixing bowl b and its rim c. The mixing bowl forming the bottom of A is circular in horizontal and elliptical in vertical cross section; its rim is slightly inclined to the outside. The pestle B is composed of the rod d with handle e and the spherical working surface f. For mixing and rubbing together powdery, friable or soft substances, it is advantageous to have the radius of the surface f small, while for crushing hard materials as ores, minerals, etc., the radius must be large. For quick and efficient work the mixing bowl b should not be more than half filled, as shown by line X.

When pressing the pestle A against the surface of the mixing bowl b and moving it round and round therein, those particles of the substances to be mixed which are compressed between the surface of b and that part of the surface f nearest to the same, are rubbed together and thus intermingled, while those particles coming in touch with the remainder of f and the lower part of d are pushed aside and forced between and above the particles not directly disturbed; those driven up the rim drop down again onto the upper layer in the bowl, an action, which, as soon as required, is assisted by means of a spatula which at the same time serves to loosen particles adhering to the walls.

In factories of pharmaceutical products often mortars of a considerable size are employed, the pestle receiving its gyratory movement from gearing driven by machine power; frequently also the mortar is simultaneously rotated round its center; scrapers following with their outer edges the inner outline of the mixing bowl and revolving with the pestle serve for turning the material over, before it is again subjected to the action of the latter. The largest mortar I saw at work had a diameter of a little over 3 ft. 4 in. These large machine mortars are not infrequently used for mixing powdered or dry substances, but more often for making pill masses, ointments, salves, creams, etc., etc.

The mixers and mills especially designed for the latter work do it usually more thoroughly and quickly than the large power-driven mortars which on the other hand have the advantage that all the parts of the mortar and pestle coming in touch with the materials to be mixed can be made of any non-corroding material, capable of withstanding any action of the substances thereon and any chemical reaction taking place in the mass being mixed, and that they can be very easily and quickly cleaned without leaving the least traces of former operations, thus being speedily ready for a new mixture.

Drum Mixer.—An old expedient to mix dry solid substances of any kind, coarse or fine, is to place them in a cask, filling it to about ¼ to ⅓ of its volume, close it firmly and then roll it slowly about on an even floor until the materials therein, continuously tumbling over and through each other, are perfectly intermingled. In the modern machines instead of the wooden cask, generally a cylindrical drum of metal is used which receptacle is rotatably suspended between two uprights of the framework carrying the apparatus. To this end, the flat sides of the drum or cask have in their centers rigidly attached thereto sockets in which the shafts, one of which carries the driving pulley or gear wheel, are fixed

These shafts and the bearings provided in the uprights in which they revolve are so arranged that the axis of rotation is horizontal and identical with the axis of the receptacle. Another arrangement for rotating the drum, especially when of a large size, is to surround it in planes vertical to its axis with toothed rings meshing with gear wheels fixed to the driving shaft rotating in bearings provided in the frame work carrying the machine; loose rollers mounted in blocks fixed to the basis of the apparatus serve usually as main or additional supports for the drum and its often very heavy contents.

The action of the drum mixer is always gentle and, if the operation is properly arranged, very fragile substances, like dry leaves as tea, flowers, seeds, crystals, etc., can be thoroughly mixed without being broken up or damaged in the slightest way. Fine powders, as well as coarser substances of great difference in specific gravity are also easily and perfectly intermingled and blended

A great advantage of this method of mixing consists therein, that, as no parts of the apparatus can exert at any point any pressure on the mass under treatment, as is the case in most other machines, the single particles of this mass cannot be compressed to form small lumps or scales which could only be separated with difficulty from the otherwise perfect mixture. For instance impalpably pulverized different pigments, fillers and driers can be mixed in the drum to a uniform shade without requiring to be resifted. For the same reason, and as the closed drum excludes the free access of air, hygroscopic substances can be evenly distributed in other matters, as for example dried malt extract in cereal flour.

The naturally slow action of the drum mixer is accelerated by arranging in its interior rows of stirrers or lifting plates fixed to and extending along the circular walls radially and parallel to its axis; in this manner a considerably larger proportion of the material under treatment is lifted at every rotation of the drum than when the interior of the latter is plain. According to the requirements of the case, the stirrers may be arranged in sequence or alternately and may be thick or thin, narrow or broad paddles, often slightly inclined towards the direction of the rotation, and the plates may extend the whole length of the circular sidewalls or only for a part, in which latter case they are arranged so that always the interstice between two plates in one row is followed by a plate of similar width in the succeeding row. The radial length of the stirrers must not exceed one-half of the length of the radius of the drum, and that of the plates must be still less because otherwise their effectiveness suffers by carrying the material too far.

It appears to be obvious that a long drum does not mix so well as a shorter one of the same diameter, as the particles contained in the former intermingle sidewise to the same limited degree as those contained in the latter. For obtaining a perfect mixture the ideal construction is here also that the length of the mixing drum is equal to its diameter. Quite a number of shapes differing from the described cylindrical one, polygonal in cross-section, sometimes cube or boxlike, are employed for the rotating mixing vessel; its axis is in some apparatus so arranged as to form an angle with the axis of rotation, and in others one or both axes are inclined from the horizontal. Convenient as these modifications may be in special cases, no real advantage accrues or is likely to accrue from any of these alterations in regard to the mixing operation.

To place the ingredients to be mixed into the drum through an opening in its circular side, for which purpose it is moved to the top, is easy, and to remove the ready mixture through the same opening, when moved to the bottom, is equally so, in regard to comparatively small apparatus, but this arrangement becomes less satisfactory and more difficult with the increasing size of the drum. Several openings placed side by side have been sometimes used, but the multiplied removal and accurate replacement of their covers for each mixing renders the charging and discharging operation

very tedious. In order to avoid this interruption of work many devices have been designed for charging and emptying the mixing drum, while revolving, from its flat end walls, one or both being provided with openings, and the drum being rotated by the toothed-ring gearing mentioned above. For instance, for charging the apparatus a funnel-like hopper is placed at its side, its bent neck reaching through the center opening in one of the flat sides, into the interior of the rotating drum; for removing the finished mixture, an inclined chute or trough suitably supported outside the drum and wide open at its top is pushed with its closed end through the center opening in the opposite flat side into the interior of the drum nearly through its whole length. Scoop-shaped lifting plates serve to drop the material raised thereby, when the drum rotates, into the inclined chute, from the open end of which outside the drum the mass slides into the receptacle intended to collect it. In another arrangement the drum is charged in the same way through the center opening in one sidewall, while it is emptied through the completely open opposite end which is closed by means of a suitable cover during the mixing operation; for quickly removing the finished mixture the interior of the drum is provided with inclined plates or spiral rings or blades so arranged as to act like a screw conveyer and thus drive the material towards and out of the uncovered end.

The drum mixer is used on a large scale for mixing grain, flour, seeds, fertilizers, ores, etc., etc. The mixing cylinder forms the rotary body of the modern continuous driers for moist grain, seeds, sand, clay, chalk, graphite, roots, pyrites, pigments, chemicals and similar materials which, by being continually intermingled, are uniformly dried. A rotary drum, when closed and heated from the outside, serves for mixing and evenly roasting coffee, cacao beans, chicory, etc., and, when provided with openings in its flat sides and fired, for roasting ores, minerals, etc., and to fuse the ingredients in the Le Blanc soda process, for cements, etc., in all cases equalizing the temperature of and reaction in the roasting or melting mixture.

The tumble-box mixer consists of a long receptacle, containing the substances to be mixed, carried on trunnions fixed to its long sides. The receptacle may be round, square or polygonal in cross-section; its ends are flat, preferably in a plane vertical to its long axis. One end is closed, while the other end is open, but provided with a tightly closing lid. For efficient work the box must not be filled above one-sixth to one-fifth of its length. The box is charged when upright; the lid is then tightly put on, and the box slowly revolved, making about 12 to 25 r.p.m. When the end containing the materials to be mixed moves upwards, they slide gradually down along that side wall which at the moment is in the lower position, to the opposite end, and are thus turned over, the upper layer becoming the lower one, while, as their movement is slanting, both layers will also more or less intermingle. The mixture is fully turned over twice during each full rotation, and, when finished, discharged by opening the cover and tilting the box. This tumble box mixes small quantities, say 30 to 40 lb., of dry colors, chemicals, drugs, powders, etc., very well, but I have never seen it used on a large commercial scale.

Continuous mixing machines are sometimes used when very large quantities of powdery products, for instance different kinds of cereal flour, the materials for self-raising flour, baking, face and tooth powders, etc., are to be mixed in a short time at lowest possible costs.

The mixing wheel, shown in Fig. 23, is an old device used in European mills. It is arranged underneath an opening in the ceiling of the chamber in which the flour mixture is collected. *A* indicates the chamber, *a* its ceiling, a_1 the opening

therein, B the hopper, the neck b of which passes through the opening a_1, C the mixing wheel and D the driving gear of C. The wheel C consists of a stationary, circular upper half c provided in the center with an opening fitting over and fixed to the neck b of the hopper B, and the rotatable, solid lower half c_1 fixed to the shaft d of the driving gear D; c and c_1 are provided with concentric rows of pegs c_2 alternately so arranged that those fixed to the lower side of c and those fixed to the upper side of c_1 pass freely through between each other, when c_1 is revolved; c_1 is carried by the brackets c_3, and the beam c_4, supporting the bearings of the vertical shaft d, by the brackets c_5; c_3 and c_5 are fixed to the casing a. The shaft d is rotated by the gear wheels d_1 and is sometimes provided with stirrers d_2. The opening of the neck b of the hopper B is usually regulated by shutters b_1.

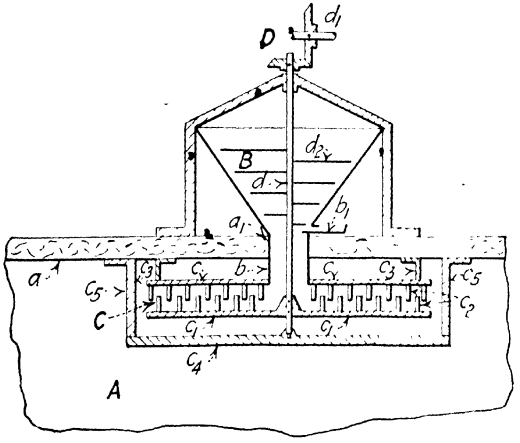


FIG. 23 Mixing wheel.

The flour streams coming from the different mills are led into the hopper B, drop then through b into between the parts c and c_1 of the wheel C and are mixed, while resting on the rotating lower half, by means of the pegs c_2, whereupon the mixture is projected by centrifugal force over the edge of c_1 into the chamber A. A homogeneous mixture can—of course—not be produced in this manner; but millers, who mixed by means of such a wheel, and bakers, who used the flour thus mixed, averred that the mixture produced in this manner was quite satisfactory for their purpose, which after all is the main thing.

The blades of more modern continuous mixers are generally based on the principle of the screw convevor, but, as already mentioned on page 531, even in these accuracy of composition and perfect mixing cannot be continuously obtained. The only continuous mixing apparatus giving full satisfaction in these respects is that in which two or more batchmixers are alternately charged by the same set of automatic weighing hoppers, and alternately and automatically discharged into the same receptacle, as soon as the mixing is perfect.

Mixing Liquids with Liquids.—In distinction from the stable cohesion of the constituent molecules of solids, those of liquids, though still adhering to each other, move freely among themselves; thus they easily separate and then combine

again. When two liquids are brought together in a vessel, they either mix, that is they spread uniformly within each other, forming a completely homogeneous mass, a solution, as for instance alcohol and water, or they do not mix, but form separate layers, as water and oil. Two liquids are miscible with each other, when the attraction of the molecules of one liquid to those of the other one is greater than the attraction of the molecules of each single liquid to those of its own kind, and they are non-miscible, when the opposite conditions prevail.

When two liquids of different specific gravity are carefully poured one after the other into a vessel, they will stand in separate layers, the heavier one at the bottom and the lighter one on the top of the heavier one. If these two liquids are miscible, the molecules contained in the two layers will immediately begin to penetrate into the other layer and continue to do so, until the two layers have completely disappeared, and a homogeneous solution is formed; the duration of this gradual intermingling—the diffusion—of the two liquids is the shorter, the smaller the difference in their specific gravity and the greater the mutual attraction of their different molecules as compared with the separate attractions. Violent agitation by means of a simple rod or paddle will greatly accelerate the perfect mixture of the two liquids. In case the two liquids having a different specific gravity are non-miscible, they will form two clearly defined layers meeting in an even plane; very rapid and violent agitation will convert them into a mixture in which minute particles in the shape of globules of the one liquid are suspended in the bulk of the other one. The production of mixtures of this class—emulsions—will be discussed later.

When two liquids—miscible or non-miscible with each other—are brought together for the sake of their chemical reaction, the more violently acting agent is usually poured very gradually into the liquid acted upon; by diligently stirring the mixing mass during the process the reaction is equalized throughout the whole mass, its intermediate phases become more clearly distinguishable, and the whole operation is accelerated and made more effective in every way. In the laboratory we mix liquids by means of the stirring rod or spatula, if contained in open vessels like a beaker or dish, and by violent shaking, if contained in a closed flask, bottle or similar container.

On a commercial scale usually the first method—stirring—is employed; the agitator serving this purpose consists in general of a vertical rotatable shaft arranged coaxially to the tank, kettle, drum, pan, montejus, cask, etc., containing the liquids to be mixed, and of the actual stirring devices fixed to the shaft, as: horizontal or inclined rods—square or round, straight or bent—vertical or inclined, plain, curved or angular vanes, propellers, etc. For discharging the ready mixture the containers are usually provided with an outlet at their bottom or the lower part of their sidewalls; but, when this arrangement is not convenient, and the vessels are to be emptied from the top by tilting or are removable from the machine, suitable lifting gear is attached to the framework carrying the driving gear of the agitator in order to raise the same out of the interior above the highest position of the mixing vessel.

When liquids are heated, which is done either by direct fire underneath or by steam led through jackets surrounding or tubes arranged within their containers, the heat is transmitted through the walls of the latter or the heating tubes therein to the liquids —with rare exceptions—at a much quicker rate than it is distributed within the latter by conduction or the currents caused by the change of their specific gravity or their quiet evaporation. Boiling and melting kettles, evaporating pans, vacuum pans, digesters, autoclaves, etc., are therefore also provided with agitators of the kind mentioned above. In order to prevent components of the heated liquid from adhering to the walls or even being scorched, these stirrers have branches—and in more severe cases actual scrapers—following the outline of or moving closely to the heating surface of the vessels.

For accelerating the mixing action it is sometimes advantageous to supply the driving gear with a reversing device so that it is possible to revolve the blades in opposite directions at will. Denser liquids naturally not mixing so easily as more fluent ones require accordingly a more powerful mixing device. The simplest way to attain this purpose is to increase the number, size or whirling power of the blades, arms or branches of the agitator. An effective construction is the double-motion mixer which consists of two agitators rotating round the same axis, but in opposite direction to each other. The inner shaft of this device is solid and carries the inner blades or branches moving in the central part of the tank, while the outer shaft consists of two tubes rotatably mounted one at the lower and the other at the upper part of the inner solid shaft and connected by the outer arms or scrapers moving along the walls of the container. The upper tube of the outer agitator rotates in bearings arranged in the lower part, and the upper end of the inner solid agitator protruding from the former in bearings arranged in the upper part of the framework carrying the driving gear of the apparatus. Between these bearings two pinions facing each other are fixed, one to the top of the outer agitator and the other to the inner one; the driving gear wheel meshing with both pinions is arranged between them, thus

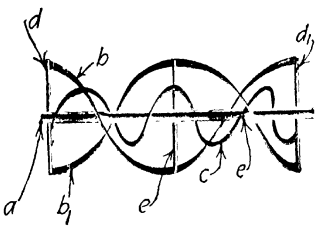


FIG. 24.—Double spiral mixer.

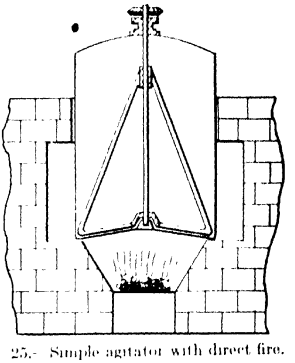


FIG. 25.—Simple agitator with direct fire.

rotating both agitators at the same time in opposite directions. The agitator must be so constructed, and its speed so regulated that no excessive splashing of the liquid can take place to the detriment of the operation, besides causing loss of the materials.

The great movability of the molecules of liquids is the reason that the mixing vessel containing them may have any size desired, controlled only by constructional possibilities and convenience. The design of the agitator and its blades and the velocity of its rotation and the power required for the same depend mainly on the consistency and specific gravity of the liquids to be mixed. When starting an agitator in a stagnant liquid mass, the resistance to be overcome is considerable, but, when once put into motion, the power necessary to revolve the agitator is very small indeed.

The various machines described in Figs. 1 to 21 may be used for the mixing of liquids, but, instead of the trough with horizontal agitator axis, usually and preferably upright tanks of a circular cross-section are employed, the shaft of their agitator being arranged in their vertical axis. A very forceful mixing device for liquids is the double spiral agitator,[1] shown in Fig. 24. d and d_1 are parallel cross rods fixed vertically to the shaft a, and passing, in case a tank forms the mixing vessel, one along its flat bottom and the other one in its upper, open part, while, if a trough is employed,

[1] Made by J. H. Day Co., Cincinnati, Ohio—Patented.

both move along its flat ends like the sidearms in Fig. 6. The ends of the spirals b, b_1 and c are mounted on the cross rods d and d_1, while they are supported in the interior by the cross rods e. The theory is, that, while the outer spirals cause a current in the mass to be mixed in one direction, the inner one does so in the opposite direction, provided that the agitator is revolved with adequate velocity, effecting a criss-cross whirling motion and thorough intermingling of the particles. The speed required for obtaining the best results in working this agitator is rather great, 50 to 80 r.p.m. The double-spiral agitator is also useful for the mixing of sifted, soft, light and very

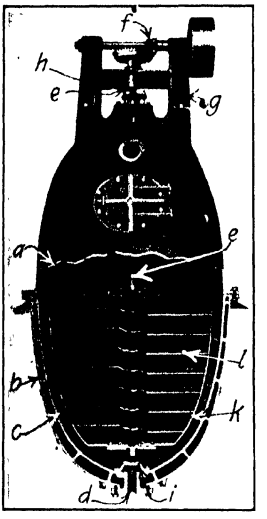


FIG. 26.—Vacuum pan.

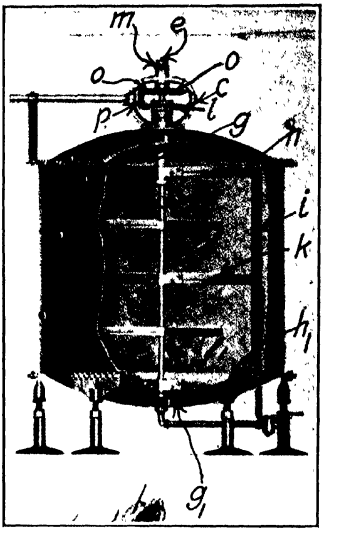


FIG. 27.—Double-motion agitator.

fine powders, as flour, face and toilet powders, etc., the particles of which flow like a fluid readily between each other when violently agitated.

Figure 25 represents in sectional elevation a simple and effective agitator frequently used in chemical factories in boiling kettles heated by direct fire. The agitator rotated at 15 to 25 r p.m. mixes very well and keeps the bottom clean from dried up and scorched material.

The vacuum pan, Fig. 26,[1] is provided with a very effective sweep agitator which greatly accelerates and equalizes the evaporation. a is the pan, b its jacketed bottom for heating by steam, coils c adding to the heating surface, d the outlet, e the shaft of the agitator, f its driving gear carried by the bracket g, h a cross piece of the latter supporting the upper end of the agitator protruding from a, i the bridge guiding the lower end of the latter, and k its sweep-arms passing closely to the coils c, while l indicates the inclined paddles forming with k the active part of the mixing device. If the sweep agitator is installed in a boiling pan or kettle having inside no heating coils or other impediments, its outside arms are usually provided with special scrapers following in outline the inner surface of the vessel, and either arranged with intervals on the opposite arms of

[1] Dopp apparatus, manufactured by Sowers Manufacturing Co., Buffalo, N. Y.

the sweep in staggered position and consisting of thin metal plates provided with sharp, knife-like front ends, or running along the whole length of the arms and formed of long, curved, knife-like narrow plates or more or less elastic rolls, pads, brushes or the like of metal wire or straps pressing against the interior wall of the vessel. It is very advantageous to provide the scrapers with devices for regulating their distance from the surface which they are intended to keep clean; but the utmost care must be taken that their construction is such that no part can loosen or unscrew while the machine is at work.

Figure 27 represents a double-motion agitator as mentioned above, the apparatus[1] being intended for the mixing of thinner liquids. The tank is provided with the outlet at its bottom and at its top with the bracket c supporting the shaft of the driving gear for the double-motion agitator. The latter consists of the shaft e on which the paddles f, f_1 are mounted, and the sleeves g and g_1 which carry the lateral arms h and h_1 connected at their ends by the vertical sidepieces or scrapers i which are strengthened by the crosspiece k passing loosely round the shaft e. The long upper sleeve g protruding through a stuffing box inside c carries at its top the gearwheel l, arranged so that the weight of the sleeves and the sweep is sustained thereby. The end of the shaft e projects through the stuffing box in the top of the bracket c and is held in position by the nut m, while its lower end loosely revolves in a guide bracket. The shaft e

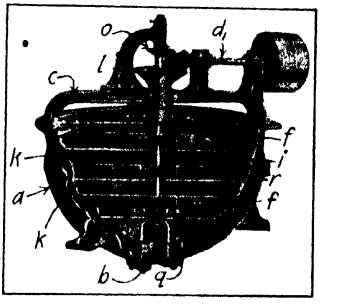


FIG. 28.- Mixer for heavy liquids

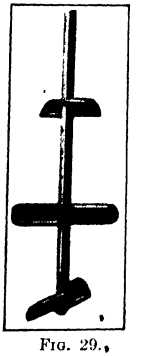

FIG. 29.


FIG. 30.

has affixed thereto within the bracket c the gearwheel o, facing the gearwheel l; the pinion p mounted on the driving shaft is arranged between o and l, meshing with both, and drives thus the shaft with paddles f, f_1 in one, and the sleeves g, g_1 with the sweep consisting of the arms h, h_1, the scraper i, and the crosspiece k in the opposite direction.

[1] Made by the Pfaudler Co., Rochester, N. Y.

A most powerful mixer for the heaviest liquid masses, while being heated, is shown in Fig. 28;[1] the kettle *a* is steam-jacketed and open at the top, the double-motion agitator and driving gear being carried by the bracket extending across the top; the agitator is constructed like that in Fig. 27, with the exception that the inner shaft has three paddles instead of two, that the side pieces are strengthened by two cross-pieces instead of one and provided with a special scraper at the bottom and smaller staggered scraper plates at the sidewall and that the diameter of the gearwheel for the sweep being double that of the gearwheel for the inner paddles, the velocity of the revolution of the latter is double as great as that of the former.

For rapidly intermingling easily miscible liquids and for keeping them in more or less gentle motion to prevent them from becoming stagnant, the propeller-shaped agitator is now generally used. This device—if rotated at a sufficiently high speed—creates an intense whirling motion which spreads very widely in a liquid mass; it is very simple of construction, easily cleaned and takes up a very small space. A small kettle of the type shown in Fig. 27 fitted with a propeller was used to mix malt extract and other liquid foods, the mass being heated to and kept at 60°C. by direct steam. The agitator made 80 r.p.m., and did its work very satisfactorily. Figure 29, is an agitator shaft[2] provided with several propeller blades which, when rotated at up to 150 r.p.m. is very effective. Small agitators of the propeller type can also be arranged horizontally in the sidewall of a comparatively large vessel used as butter-milk machine, ice-cream mixer, starter can, etc., in dairies. The thrust of the propeller is directed across the tank and produces a thorough circulation at a speed of about 300 r.p.m.; only very little power is required.

In cases where it is desired to give an upward tendency to the circulation of the liquids in the center of the mass, a propeller of the marine type is used and surrounded as shown in Fig. 30, by an open cylinder or drum[3] in the lower part of which the former is situated. The agitator is especially adapted for rapid mixing of light liquids and requires for thorough work a speed of 25 to 50 r.p.m. For very thick liquids instead of the propeller a screw conveyor rotating within the drum is employed with advantage; in case the mass is to be heated at the same time, the drum is constructed as a radiator forming a hollow shell or a cluster of steam tubes as for instance in the crutcher for melting and mixing soap masses. Figure 31[4] represents a very powerful apparatus of this class in which conveyor screw and drum are rotated in opposite direction. *a* is the steam jacketed kettle; *b* is the conveyor screw fixed to the center shaft, which rotates in the sleeves *d* and d_1 carrying the drum *e*, sweeps *f* and inclined cross pieces *g* stretching from *e* to *f*; screw *b* rotating in one direction and the drum *e* with the sweeps *f* in the opposite direction.

Liquids which easily combine, as for instance hot and cold water, liquids plain and containing chemicals dissolved, are frequently mixed in a continuous manner by leading them in the required proportion through separate pipes into a wider common tube or box in which they encounter cross bars or baffle plates often arranged in a screw-like fashion.

Mixing Liquids with Solids.—An absolute homogeneous mixture of liquid and solid substances can only be obtained if the latter are soluble in the former, even then in most cases after standing we find the strongest and thus the heaviest solution at the bottom, getting gradually weaker toward the surface. Water-soluble chemicals, which are not affected by heat, are generally dissolved by introducing into the water direct steam, which, entering with great velocity,

[1] Made by Sowers Manufacturing Co

[2] These agitators are made of any metal or glass-enamelled by the Pfaudler Co., Rochester, N. Y.

[3] Made by the Pfaudler Co., Rochester, N. Y

[4] Dopp apparatus, manufactured by Sowers Manufacturing Co., Buffalo, N. Y

causes a rapid movement in the mass, while heating it at the same time by being condensed, thus greatly accelerating the dissolution. If more valuable liquids, as alcohol, ether, acetone, chloroform, carbon disulphide, etc., are used as solvents the operation is performed in a closed pan or kettle provided with an agitator, and, in case heat is to be used for assisting in the operation, with a steamjacket or steam coils and with a reflux condenser.

In cases where heat may cause damage to the product or is to be avoided for practical or economical reasons, the vessel, in which the solids are to be dissolved, is provided with an agitator adapted to keep the undissolved particles, prone to settle at the bottom in continuous motion. An apparatus[1] is especially designed by Werner and Pfleiderer for this kind of work, in which the effect of the agitator, consisting of a propeller or tangential wheel, is greatly enhanced by the peculiar egglike shape of the mixing tank which in its lower part forms a hemisphere and in its upper part a truncated cone. The propeller revolving at a high speed forces the liquid and the solids

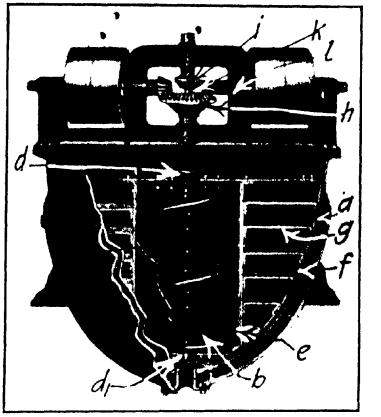


FIG. 31.—Double-motion kettle.

suspended therein with great violence from its center sidewise towards the spherical wall, thus driving both upwards against the inclined wall where the current is broken, (if needed, by baffle-bars), and directed towards the axis of the agitator, and then draws the mass in again from this central part for repetition of the cycle, until the operation is finished.

Solids which are to be intimately mixed with a liquid in which they are insoluble, must be in a finely pulverized state. In case that the adhesion of the molecules of the liquid to a solid, otherwise unaffected by the same, is greater than the cohesion of the liquid molecules to each other, the solid is wetted by the liquid, and both are then easily mixed. When a small quantity of such solids is to be suspended in a comparatively large quantity of liquid, the simple mixers shown in Figs. 24, 26, 27 and 30 are used with advantage, the agitator blades being arranged so that their surfaces point in the direction of the rotation, downwards when the solid particles are heavier, and upwards, when they are lighter than the liquid.

If only a small quantity of liquid is mixed with solid matter, creams, pastes or pulps are formed of a stiffness and consistency corresponding to the proportion of the latter to the former. The machines Figs. 4, 6, 7, 18, 19, 21, 26, 28 and 30 and similar

[1] Made by the Baker-Perkins Manufacturing Corp., Saginaw, Mich.

mixers usually serve this purpose very well; for making a fine mortar, sanitary pastes or the like, and mixing paints, an edge mill is often used, in which a pair of stone or metal rollers of large diameter, loosely revolving on a horizontal shaft turned round the vertical axis of the machine, press, squeeze, flatten and, by thus crushing and disintergrating the smallest lumps and particles of solid matter, thoroughly mix the mass which is contained in an annular pan arranged in the circular path of the rollers. The pan may sometimes also be rotated opposite to the direction of the latter round the same vertical shaft. In regard to pastes, etc., it may be said in general that a certain composition and quantity of solid matters can only retain—without any separation after standing for some time—a distinct maximum of a liquid, the amount being mainly dependent on the fineness of the solid particles, the size of their interstices and their capillarity.

It is always advisable to charge powdery matters gradually into a liquid while the agitator is working, and only to add a fresh portion, after the previous one has been distributed therein; if the quantity of the liquid is large, and the solid particles are inclined to combine, when wetted, to lumps and knots, the whole mass of the solid matter is first mixed with a small portion of the liquid to form a thin paste which is then gradually added to the rest of the liquid whirling round in the machine.

In cases where the solid materials are not wetted by the liquids with which they are to be mixed, more energetic means must be employed, and the operation must be continued for a longer time in order to convert them into a smooth mixture which is as homogeneous as possible according to the nature of the ingredients. For intimately mixing and blending oils and fatty substances, varnishes and the like with powders of any kind, with watery solutions of salts, acids and other chemicals, and with similar materials in the manufacture of butter, margarine, cosmetics, sanitary and color creams and pastes, rubber imitations, scouring soaps, shoe, stove and metal polishes, printing inks, lead-pencil masses, ointments, salves, chocolates, candy, chewing gums, etc., the two-blade mixer Fig. 19 and the double-motion agitator have proved very useful machines. Small quantities of these products are frequently prepared in suitable containers which are changeable; after having been charged, the single receptacle is placed on a rotating platform, and an energetic agitator lowered into the mass to be mixed by means of a mechanism arranged at the support of the platform and driving gear of the machine.

Pharmacists often prefer to prepare their ointments, creams, salves and pastes in a machine mortar or in a small stone mill especially equipped for this purpose. It is claimed by some experts, that such preparations, when mixed in that manner, are smoother, softer and of a more homogeneous nature than those made in mixing machines, because the molecules of the substances to be mixed—so different in their nature from and even repelling each other—are finely ground together under pressure, also the smallest knots and unevennesses being completely smoothed out, while in the mixing machine only a forcible intermingling of the particles could take place. For the same reason, the finer oil colors for coaches, furniture, art paintings, printing inks, pastel colors, and similar products are usually made in stone mills, the under runner of which makes about 100 r p.m.; the feeding hopper is frequently constructed as a preparatory mixer, being fitted with a suitable agitator; for rather stiff pastes and colors it is sometimes advantageous to make arrangements to feed the mass to be mixed into the mill under pressure. For the products described, but especially for printing inks, often roller mills, usually having three water-cooled rollers of iron or granite, are also employed. The mixture for chocolate mass, consisting of cacao powder, fat, sugar and condiments, is generally produced in an edge mill the stationary pan of which is heated by steam or hot water.

Much attention has been given to the development of concrete mixers. In the manufacture of artificial stones, concrete building blocks, drain pipes etc., in which

fine sand, trass, gypsum, pigments and other filling materials are incorporated with cement and water, it is—in order to obtain a good result and to prevent the formation of hard lumps in and the premature hardening of the mass—the best plan first to thoroughly mix and intermingle all the solid ingredients while in the dry state which may be done in any machine described above for pulverized materials, and then quickly to introduce the water in shape of a strong spray covering the whole exposed surface of the mixture while still being agitated. For mixing coarse sand, gravel, pebbles, stone chippings, etc., with cement and water for producing concrete for roads, dams, water reservoirs, etc., the most frequently used machine is a rapidly revolving, inclined drum mixer provided with means for quickly charging and discharging a batch; in order to bring the concrete in the best possible state for hardening on its bed, each batch must be comparatively small, it must be quickly handled, and the operation rapidly repeated.

In the manufacture of explosives, smokeless powder, celluloid, etc., the two-blade mixer, Fig. 20, in which each shaft carries two symmetrically arranged, elliptical blades has been prominently used for a considerable time; its advantage is that the peculiar construction of these blades and the low speed at which they are worked, contribute considerably to the safety of the operation, as for instance mixing different kinds of guncotton in a moist state or blending them dry with a solvent. The machine is usually provided with a jacket for cold and hot water or steam, and, in case that the contents are to be dried at the necessary low temperature and the solvent is to be regained at the same time, the top of the machine is closed by a tight lid connected to a condenser and vacuum pump, the operation thus being performed in vacuo.

Mixing and Kneading Dough for Bread.—Ordinary dough is prepared by fermentation from flour, salt, yeast, and water as main ingredients to which, in order to stimulate the activity of the yeast and to improve the taste, flavor, composition and appearance of the finished article, varying smaller quantities of milk, dried milk, fats, sugar, malt-flour, malt-extract, cornflakes, yeast-feeding salts, spice, etc., are added. The quantity of water used for the dough is between 50 and 65 per cent of the flour contained therein. The soluble ingredients are usually dissolved in a small portion of the water, and the yeast finely distributed in another one; all the components of the dough are then combined and thoroughly mixed and kneaded, that is pounded, pulled, pushed, drawn out, stretched and folded over again until the resulting dough has the required consistency, elasticity, and homogeneity.

The dough is then put aside in a warm room for fermentation and, after having risen, scaled off and molded into loaves, which, after again undergoing a short time of fermentation, are baked. Wheat flour produces a white, very light, spongy, palatable and easily digested bread which for these reasons is preferred and more generally used in civilized countries. These good qualities are due to the wheat flour containing a considerable quantity (9 to 12 per cent) of gluten in a quality characteristic of this cereal. When dough is made of this kind of flour, the water dissolves its soluble components, penetrates through and softens the starch grains and will be absorbed by the gluten in a quantity equal to about double the weight of the latter. The gluten is thereby converted into a soft, swollen and yet firm and cohesive mass of very considerable elasticity. By kneading the dough the gluten is drawn out to strands and then widened to bands, which, crossing the dough in all directions, will finally form, when combined at their edges, a complete sponge-like network containing all the other ingredients of the dough and possessed of such a strength and resiliency as to retain therein the carbonic-acid gas developed by the subsequent fermentation of the sugary components. In a perfectly, an ideally kneaded dough

these cavities will be of equal size, have walls of equal thickness and resiliency and contain equal amounts of the other ingredients; it is obvious that, if only to approach this perfection, the kneading must consist of drawing, stretching, pulling and sidewise combining only, and every tearing and separating action must be avoided; in short, it is necessary to knead the dough in bulk.

Some 50 years ago nearly all bread dough was mixed and kneaded by hand, and the bread baked on the hearth; only in the bakeries for large garrisons, navy yards, hospitals, etc., kneading machines were employed; they were usually more beaters than mixers and required a very considerable amount of power for working the stiff doughs necessary for hearth bread. The most successful kneader then used had an agitator consisting of two four- or six-armed side pieces arranged at the shaft so as to rotate closely to the flat ends of the half-cylindrical trough and connected at their ends by diagonal rods, two crossing from each arm of a sidepiece, one to the next arm at the left side and the other one to the next arm at the right side of the opposite sidepiece. In consequence of this arrangement the rods could only approach closely to the circular wall of the trough at their joints with the side arms. An agitator

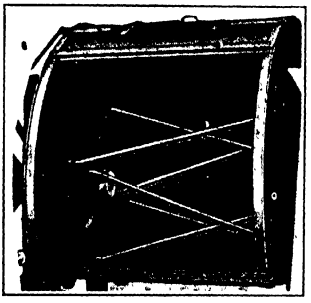


FIG. 32.—Double mixer.

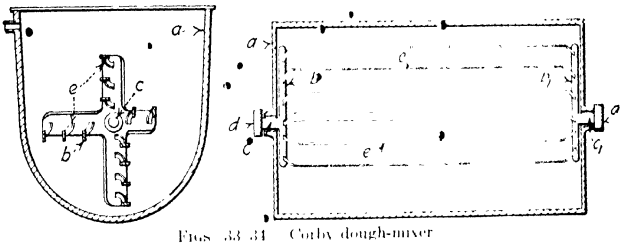
quite similar to that described is shown in the dough mixer, Fig. 32,[1] which is especially recommended for the development of gluten in heavy doughs. In those times the bakeries were small shops, too small for a steam-power plant; in the seventies of last century the small gas engine of 2 to 10 hp., so useful for numerous small establishments, came on the market and contributed greatly to the quick introduction in Europe of the two elliptic-blade mixing and kneading machine, Fig. 19, which—contrary to the machines already known—required comparatively little power. This machine is—as has already been stated above—a quick and excellent mixer; it produces a very good dough for hearth bread in a very short time, 4½ to 5 min., and at a low speed, 7 to 10 and 12 to 20 r.p.m. respectively for the two agitators, the actual power used in a two sack machine (for 560 lb. of flour) being at the most 5 to 6 hp.

But the dough maker must be an experienced man, capable of judging, when the dough has reached its proper consistency for a good, well-risen loaf and stop the machine at the right moment, the danger being that after longer kneading it would become soft and putty-like and yield only a comparatively small and sodden loaf. The reason for this injury to the dough by overkneading it in this class of machine is that not only small bits are torn from the already finished dough when pressed along the circular surfaces of the double trough by the blades rotating closely along it, but also a considerable portion is cut away on the saddle while being passed over

[1] Made by J. H. Day Co., Cincinnati, Ohio.

from one-half to the other one, twice at each revolution of the blades; the fully extended gluten strands thus after some time become completely disintegrated and give the dough the appearance as if a weak flour had been used. This explanation is confirmed by the fact that, when a thus over-kneaded dough stands for some time, it will partly regain its strength, apparently in the measure as the torn gluten ends are able to join again, due to expansion by fermentation.

For hearth bread, only a limited quantity of water can be kneaded into the flour, 49 to 55 per cent according to its strength, because, if more were used, the dough, though perhaps showing a good shape after molding, would flatten out in the oven like a pancake; also any appreciable addition of fat (shortening) or sugary matter must be avoided, because, if used in larger amounts, they naturally diminish the strength of the dough. Doughs containing a large proportion of water (say 60 per



FIGS. 33, 34.—Corby dough-mixer.

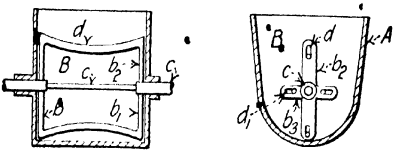
cent), or of the last ingredients mentioned (say 2 per cent) are placed into pans the sides of which, upholding the dough mass during baking, not only prevent it from running, but cause it to creep upwards and thus produce a very light loaf. These light doughs require, as compared to the heavier ones, in the two-blade machine, Fig. 19, a higher speed, 10 to 18 and 20 to 36 r.p.m. of the two blades and a longer time of kneading, 10 to 20 min., and the result is not so good as in a modern high-speed kneading machine which is now mostly used in the United States where the bakers, having the best wheat flour in the world at their disposal, are bent on producing for us also the very best bread by adding a remarkable amount of fat and sugary substances (about $2\frac{1}{2}$ per cent of each), milk powders, etc., and a correspondingly larger quantity of water.

According to the Corbys,[1] the inventors of this method of dough making, their kneader consists essentially of a receptacle, in which a beater comprising a pair of spiders and a series of longitudinal bars extending between the latter revolves at a high speed. Figure 33 represents a top view and Fig. 34 a cross-section of the original design: a is the kneading trough having a half-cylindrical bottom; b and b_1 are the spiders fixed to the trunnions c and c_1 provided outside a with the gear wheels d and d_1 for driving the agitator. The four arms of the spiders b and b_1 are of different length, carry a different number of beater bars e and are arranged in line at the trunnions c and c_1 so that the bars e extending between them are parallel to the axis of rotation. It will be noted that also the bars e nearest to the circular wall of a do not approach it closely. The driving gear is so arranged that the beater is driven at a high speed which means for this class of machine 45 to 80 r.p.m.

A short time after the materials have been placed in the trough and the beater is running at a high speed, a thin dough-like mixture is formed, having little tenacity and a rough appearance; then the rapidly rotating beater bars separate small portions

[1] W. H. CORBY and CHARLES J. CORBY, U. S. Pat. 629,239, July 18, 1899, of Process of Dough-making; 639,889, Dec. 26, 1899, for Machine used for this process.

from the main mass by centrifugal force and throw them about; with the increased tenacity caused by the quick development of the glutenous condition of the dough, these separate portions adhere to each other and to the main part more and more, until the whole mass extends in strands and sheets from bar to bar of the beater; the centrifugal force will drive all these sheets and strands always farther away from the axis of rotation, so that almost the whole bulk of the dough is worked by the outer bars and against the wall of the trough which tends to retard its passage. The dough will thus be drawn out to thinner or thicker sheets between the bars and the wall according to their smaller or greater distance from each other. Free from the wall in the upper part of the trough the sheets are folded up and then caught again between the bars and wall to undergo the same treatment which is repeated until the dough is finished, forming a perfectly smooth, creamlike, homogeneous and very tenacious mass which is the foundation of a well fermented dough and a very light[1] bread baked therefrom. The operation is completed in 20 to 30 min. The improvements made in this class of



FIGS. 35-36.—High-speed mixer.

kneader refer mainly to the strengthening of the beaters, the trough, gearing and frame work supporting the machine, as they are naturally under immense stress and pressure, especially during the later part of the operation.

Figure 35 shows the longitudinal and Fig. 36 the cross-section of the trough A and dasher B of a modern high-speed kneader,[2] in which the spiders b, b_1 of B consist each of two pairs of arms b_2 and b_3 arranged vertically to each other, and are rigidly mounted on the central driving shaft c passing through the whole length of the trough. The longer arms b_2 reach closely into the corners of the half-cylindrical bottom and the sides of a and carry at their ends the strong beater rods d bent in a curve towards the center of the driving shaft c, while the similarly curved beater rods d_1 are fixed to the ends of the shorter arms b_3. The inwardly curved beater rods d and d_1 cause the dough mass to be drawn towards the middle part of the machine and thus greatly facilitate and increase the effect of the working of the dough in bulk.

In another prominent machine of this kind, the agitator and trough of which are shown in Fig. 37[3] two beaters a and a_1 are arranged one within the other, the beater a being mounted on trunnions b and b_1 revolubly fitted in tube-like trunnions c and c_1 carrying the outer beater a_1. To the end of the trunnion b protruding from the tubular trunnion c is affixed the spurwheel d, and to the tubular trunnion c_1 on the opposite side of the machine the spurwheel d_1 which is somewhat larger in diameter than d. The spurwheels d and d_1 mesh with pinions e and e_1 fixed on the driving shaft f of the machine so that the beaters a and a_1 are rotated in the same direction, but the inner one at a higher speed than the outer one. The outer beater a_1 consists of two equal, symmetrically arranged parts of the peculiar shape shown in the illustration, the inner beater a is formed of two curved blades corresponding to the shape of the inner cir-

[1] For illustrating this point I may state that I found by repeated careful experiments that the proportion of the size of a good English Cottage loaf (hearth bread) to the volume of an equal weight of water is = 234 : 1, while the same proportion for a good class American loaf is = 4 : 1.

[2] W. J. TREVIS'S, U. S. Pat. 1,041,908, Oct. 22, 1912. Bakers-Perkins Mfg Corp., Saginaw, Mich.

[3] F. NOTZ and J. MCBRIAR'S U. S. Pat. 831,372, Sept. 18, 1906. Manufactured by American Oven & Machine Co., Chicago, Ill.

cumference of the curved part of a_1, sufficient space being left between the two for efficiently working the dough.

The proportion of the revolutions per minute of the inner to those of the outer beater is about 3 : 2; for the slack pan-bread-dough of the large bread factories 60:40 r.p.m. is recommended. The peculiar construction and working of this agitator tends

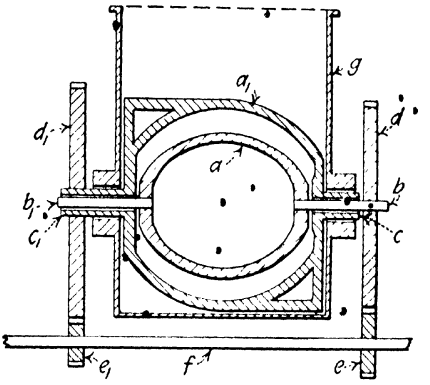


FIG. 37.—Double-beater dough mixer

to make the machine a somewhat better mixer; but its main point consists therein that the stretching of the developing glutenous dough does not take place between the circular wall of the trough bottom and the outer blades, but in consequence of the more rapid rotation of the inner beater chiefly between the latter and the outer one, a circumstance which appears to be of decided advantage.

The working capacity of these high-speed kneaders is naturally much less than that

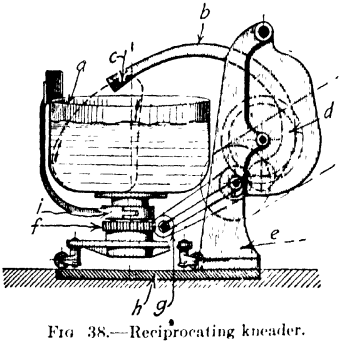


FIG 38.—Reciprocating kneader.

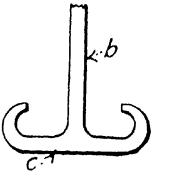


FIG. 39.

of low-speed machines; for in general, the higher the speed, the smaller is the working capacity of the machine for the same mixture and result. The violent action on the dough of beaters revolving at a high speed will raise its temperature, in hot weather even to an injurious degree; some constructors seek to prevent this occurrence by introducing cold air into the dough and the interior of the kneading trough, and others by passing cold water through a jacket surrounding the latter, while bakers sometimes

use the rough but simple remedy of dropping a few pieces of ice into the mixing mass. The time necessary for obtaining a perfect dough in high-speed kneaders is long, 15 to 20 min. and even more, and the amount of power required very great, 20 to 25 hp. on the average for a machine mixing 1,000 to 1,200 lb. of dough at 50 to 60 r.p.m. of the agitator.

In Europe where a low price of ordinary bread always was a paramount economical necessity, the costs of producing the dough forms naturally an important factor; the endeavor of the designers of kneading machines was therefore to devise a construction which requires less power even than the two blade kneader, Fig. 19, and in which the operation can be performed without the supervision of an experienced dough maker. This problem seems to have been solved by the reciprocating arm-kneader of which Fig. 38 shows an example. In this machine the dough is worked in the circular rotating pan *a* by means of the reciprocating arm *b* ending in the crosspiece *c* which consists of two lateral hook-like appendages as shown in Fig. 39.

The action of the arm *b* and the crossbar *c* the course of which is shown in Fig. 38 in dotted lines, is a remarkable imitation of the old-fashioned kneading by hand, a fact which probably aided greatly in the introduction of the machine. The driving gear *d* is supported by the strong frame-work *e* arranged at the back of the pan *a* which, provided with the toothed ring *f*, is rotated by gearing *g* carried by a bracket fixed to *e*. Being removable, the pan *a* is provided with wheels, and, when disconnected from the machine, serves as a container for the dough during its fermentation, thus saving the emptying of the kneading trough necessary in other machines. When kneading is to be done, the pan is pushed, after the arm *b* has been raised, on to the bed-plate *h* and into the hinged locking device *i*, which holds it in its proper position in regard to the driving gear. The arm *b* draws the dough out very gently, making it loose, and works only on that portion which it reaches on its downward stroke, leaving the rest for a short time undisturbed so as to allow the gluten of the flour to contract and to connect, which is considered to contribute greatly to its development.

As the arm *b* does not throw or splash the dough about, the working capacity of the machine is very great indeed, while the flat bottom of the pan and the peculiar arrangement of the kneading arm allows also a very small amount to be efficiently treated; thus the working capacity of a pan of 560 liters cubic contents would range between 50 to 500 kg of dough.

The kneading arm of this machine makes 24 to 30 strokes per minute, while the pan does 4 to 6 revolutions in the same time. As only a portion of the dough is kneaded at each stroke, the power required is naturally very small, even considerably less than that for the two-blade mixer, Fig. 19; for a size suitable to work a batch of about 1,200 lb. of dough 3 to 5 hp. are quite sufficient. Kneading a batch of dough in this machine takes about 10 min., and, as the action of the agitator is very gentle, the elasticity and tenacity of the mixture do not suffer by over kneading. In another kind of reciprocating arm-kneader which is much used in England, only the inclined, separate bottom of the pan is rotatable, while the upper part is stationary, the ready dough being discharged through a door provided in the latter.

Very large kneaders intended to work 20 to 25 bbl. of flour in one batch have been constructed and tried, but without success; for general practical and economical reasons I consider in regard to the above described types of kneaders a working capacity of 1,200 to 1,500 lb. of medium dough as the most favorable one.

For smaller bakeries where 1 to 2 bbl. of flour form a batch, simple single-blade mixers, for instance that shown in Fig. 18, will usually do the work with satisfactory result and at the costs of little power. Also a special drum mixer in which a number of rods, extending parallel to the axis from one flat side to the opposite one of the drum, act as beaters, is employed for making dough; it is only suitable for smaller batches and slack doughs.

Cake doughs are made from flour with such large additions of fat, sugar, raisins, currants, fruit jams, condiments, etc., that the qualities of the flour and especially of its gluten loose their prominence. Any mixer, which is liquid-tight and mixes quickly and well, will therefore do the work, for instance a small two-blade mixer or a double-motion agitator of simple construction. In smaller bakeries and confectioneries usually simple agitators rotating round a vertical axis and adapted to be lowered into the mixing bowl or pan are employed, the agitators as well as the mixing vessels being exchangeable. Agitator blades of different type and size and mixing vessels of different shape and capacity are

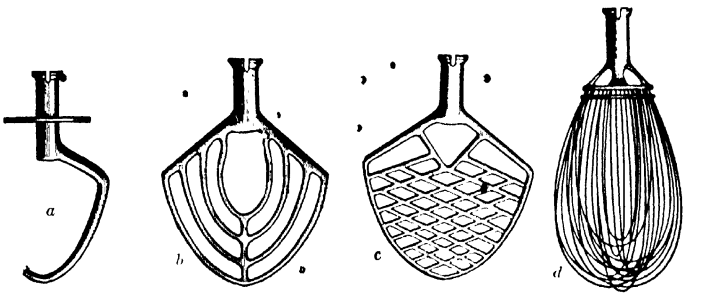


FIG. 40.—Typical cake-mixing blades.

supplied, and the driving gear has three or four different speeds, so that every probable kind and size of cake dough can be produced in the single machine. Figure 40[1] shows a typical set of blades for this class of mixer; *a* is intended for roll or pie dough, *b* for heavy cake, almond paste, sugar icings, etc., *c* for mashing vegetables and fruits, for sponge and soft-cake batches and *d* for whipping eggs,

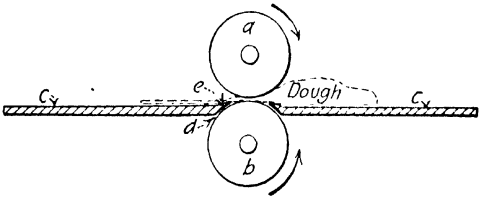


FIG. 41.—Dough-brake.

cream, mayonnaise, dressings, etc. The blades are rotated the quicker, the thinner and more fluid the mixture to be treated.

Biscuits, crackers and similar flat and thin cakes which are intended to keep well, contain, after having been quickly baked and, if still too moist, dried, only 3 to 9 per cent of water against about 40 per cent in bread which is eaten fresh; thus it is not only advantageous, but necessary that the original dough is made with as small a quantity of water as possible. The ingredients are first mixed in a kneading machine suitable for heavy dough; in consequence of the absorption

[1] Mixer manufactured by Read Machinery Co., York, Pa.

of water by the starch and gluten of the flour the mixture will after a time become so stiff and hard that its further treatment in the machine becomes useless and even impossible; in this way neither the soluble and insoluble components, as sugar, salt, fats, condiments, etc., can be thoroughly intermingled with the water and flour, nor the glutenous condition of the latter fully developed.

This purpose is attained, and the kneading of the dough finished by pressing and drawing it out to a long sheet between two heavy rollers—the dough brake—by then folding it up, letting it pass through the brake again and repeating these operations, until the resulting dough has the required evenness, smoothness, cohesiveness and elasticity for its thin sheets to be cut and baked into perfect products. The dough-brake is an evolution of the rolling pin and consists essentially, as diagrammatically shown in Fig. 41, of two parallel, superimposed rollers *a* and *b* and the stationary table *c* which contains in its middle part the opening *d* under which the roller *b*, the feed roller, protruding somewhat therefrom, is rotatably fixed, the long edges *e* of *d* being formed to serve as scrapers for *b*.

The rollers rotate in opposite directions so that the dough sheet travels through between them; in order to work from either side of the table, the driving gear is fitted with devices for easily and quickly reversing the rotation of the rollers; their distance is adjustable for producing a dough sheet of pre-determined thickness. The rollers used in this machine are usually of steel, smoothly polished and have the same diameter which is made the larger—and thereby the weight of the roller the heavier—the greater the difficulty with which the dough is worked. The power necessary for driving the machine is comparatively small; a brake having rollers of 2 ft. 2 in. length and 10 in. diameter (weight about 580 lb. each) requires only about 2 to 3 hp. The output of the machine greatly depends on the skill and experience of the operator.

Macaroni, noodles, vermicelli and **similar products** contain also only a small quantity of moisture, about 9 to 12 per cent, and therefore as little water as possible for obtaining a good result is used in the dough. The flour for the same must be very strong, and its gluten developed to its full viscidity and elasticity so that the dough can be easily divided and shaped by means of dies under high pressure in a screw, or hydraulic press, and that the products thus obtained, tubes, strings, threads, bands, figures, etc., retain their shape during drying and do not break or are damaged when packed. The dough can, of course, be worked like that of biscuits first in a mixer and finally in a dough brake; but, as no sheeting is required, usually the manufacturers of those articles employ instead a kind of edge mill which, working the dough under high pressure automatically, saves the considerable amount of manual labor and attention necessary for the dough brake. This apparatus[1]—the rotary roller pan—consists of a flat circular pan rotated round a vertical shaft, arranged in its center, by means of a toothed ring fixed concentrically to the bottom of the pan and meshing with the driving gear of the machine, and of one or two heavy rollers loosely mounted on shafts fixed to the framework radially to the pan and rotated by the dough passing underneath on the bottom of the latter when revolving. The dough is continuously turned over by a plow-like scraper and crushed, ground together and kneaded under the pressure of the very weighty rollers the pressure of which may be enhanced by strong springs either pressing the vertically movable pan against the rollers mounted on stationary supports or *vice versa*. The working capacity for a pan of

[1] Made by the Baker-Perkins Mfg Corpn., Saginaw, Mich.

about 5 ft. 6 in. diameter is a batch of 250 to 300 lb. of flour, requiring about 5 hp.

Mixing and Incorporating Plastics.—Substances which are of a plastic nature and capable of imparting this quality to a limited amount of solid or liquid matter, have usually so high a degree of cohesiveness that they can only be mixed with the other ingredients with great difficulty, considerable pressure being necessary to overcome their toughness. Two-blade machines as shown in Figs. 15, 17, 19 and 21, the double-motion agitator, the combined double motion and screw agitator, Fig. 31, and similar machines are in most cases capable of doing this work satisfactorily. Heat must frequently be employed for assisting in the operation. In cases in which the pressure during mixing must be especially great, for instance when substances, which like india rubber possess besides great cohesiveness an exceptional high degree of elasticity and tenacity, rollers like those described for the dough brake, Fig. 41, are employed with advantage. A two-blade machine, Fig. 17, especially constructed for this kind of work in which the active surfaces of the blades, while retaining their diagonal position in the double trough, form curved instead of even planes, has been found very useful in the manufacture of all kinds of rubber goods, balata, linoleum, artificial ivory, art stones, and similar products. When, as is frequently the case, fine powdery substances are to be incorporated into tough rubber-like masses, it appears to be advantageous to add the powder gradually in the measure as it is taken up, spreading it widely over the whole mass exposed in the machine.

Whisking and Emulsifying.—By very rapid and violent agitation cream, eggs, their mixture with sugar, thin batters made of flour, milk, eggs, etc., sauces and mayonnaises consisting of egg yolks, oils, vinegar and flavorings and similar mixtures comprising gelatinous and fatty ingredients and water, are whisked, whipped or beaten into light perfectly intermingled and blended masses which, in case the gelatinous components are present in sufficient a quantity to be capable of retaining the air whipped into the mixture in the shape of small bubbles, are foamy or spongelike. Figure 10*d* shows a simple eggwhisk made of a bunch of wire loops which is rotated at 100 to 150 r.p.m. and gives for small as well as large quantities a good result.

Very effective mixers of this class are constructed according to the double-motion principle, each of the agitators consisting, if the mixing vessel is a bowl or the like having a spherical bottom, of half-circular bows of strong round wires symmetrically arranged round the two hubs, or, if, that vessel is a trough with half-cylindrical bottom, of rectangularly bent strips of band steel connected by crosspieces, all presenting their narrow sides in the direction of the rotation. The agitators revolving in opposite direction to each other are driven at 90 to 200 r.p.m.; the inner one frequently a little quicker than the outer one. The size of the mixing vessel must be very large in regard to its real working capacity, as the materials under treatment are much thrown and splashed about, and as the volume of the mass increases by the inclusion of air to a remarkable degree; for instance 1 qt. of cream may form, after having been properly whipped, 3 to 4 qt. of whipped product. The nature of the ingredients prevents the employment of large-sized apparatus of this class; a whisk capable of beating up 200 eggs with sugar will have a total capacity of about 10 gal., which is about the limit size employed.

The product of the even distribution of oleaginous matters in shape of minute globules in a large quantity of water by means of still more forceful agitation than

that used in whisking forms an emulsion, the name being derived from the best-known representative of this class, milk, which consists of a watery solution of milk sugar, proteids and salts in which about 3½ per cent of butterfat are finely suspended. Mechanical means alone are not sufficient to produce an emulsion which would keep any length of time; it is necessary that the water with which the fatty substances are to be mixed contains in solution proteids, gelatinous compounds, sugar, glycerin, soap or other colloid chemicals. The mixers used are the same as those employed for whisking; only that the agitators are rotated at a higher speed, from 500 to 1,500 r.p.m. as the case may require. A most efficient emulsifier for commercial use is a rather flat propeller-agitator, the blades of which form an angle of 5 to 10° with the horizontal and are revolved at a speed of 1,000 to 1,500 r p.m., the oily substance being very gradually added through perforations in the hollow shaft.

SECTION XVI

SAMPLING

By Donald M. Liddell[1]

Definition.—Sampling is the process of obtaining a small quantity of material which shall be representative of the average of some large amount. Theoretically each portion of a sample however small should itself be representative of the large body, but in practice this cannot be obtained owing to the impossibility of reducing all of the sample to a molecular state of subdivision

Owing to the difficulties of getting a small sample of a few ounces in weight to represent a large amount of material, the sampler will ordinarily divide a large shipment into several lots, each to be sampled and settled for separately.

The importance of proper sampling is rarely correctly estimated The utmost care is ordinarily given to all the operations of a chemical laboratory. Large sums are spent in its proper equipment and high salaries paid to the chemists employed without regard to the fact that the accuracy of the analytical work is primarily limited by the accuracy of the samples furnished to the laboratories. It appears to be the customary assumption that any $3 a day man can prepare samples for a $20,000 staff of chemists As an interesting commentary in how little is ordinarily thought of sampling, it was not until the eleventh volume of the transactions of the Institute of Mining Engineers that any article appeared on sampling

The ways in which the accuracy of a sample can be vitiated are many, but a proper understanding of the underlying principles will enable one to see the mistakes and to correct them. On the other hand, one of the easiest ways to point out the underlying principles is to describe certain specific errors in sampling and to show the cause and the cure, so that in large measure this paper will be a discussion of the errors of sampling.

In the sampling of solid materials we come immediately upon two classes those which can be crushed and those which must be drilled, sawed or filed. In sampling materials of the first class where payment must be made on the value of the shipment the question of moisture is the first to present itself and is probably one of the greatest sources of error. After weighing the material the moisture sample must be taken as quickly as possible, and must be large enough to represent the whole mass correctly yet small enough to permit of drying the entire moisture sample. The reason for this latter stipulation is that it is impossible to crush and mix a moisture sample because mechanical work performed on it alters the moisture content. The moisture sample must not be representative of fine material alone or of the coarse material only, but must be fairly representative of both classes in their proper proportions. Usually a finely divided material will carry a greater proportion of moisture than will coarse lumps, and it is ordinarily the tendency of the sampler, owing to the small size of the moisture sample (comparatively) to take an undue proportion of fines, since even one lump of ore appears as a mountain in the moisture sample.

[1] Weld & Liddell, Engineers and Economists.

Ordinarily a moisture sample is said to have been dried at 212°F., even though the temperature of the drying oven may have been allowed to run up even to 240°. This matter of drying temperature is one of importance for the material may contain water of crystallization not completely given off at 212° or may contain salts where the acid radical is more or less completely expelled at temperatures only slightly above 212°, or the "moisture" may be some such substance as free sulphuric acid. At any rate it is important that the moisture sample and the final sample for the laboratory should be dried at the same temperature and if the material is hygroscopic care must be taken to keep it in a stoppered bottle or other watertight receptacle. It should also be realized that practically all crushed pulps are hygroscopic, and if any sample is to be re-analyzed after it has stood for some time in paper or cloth bags, it should be dried first.

In drawing the original moisture sample from any material whatever it is an elementary proposition that the sample must not be taken from the immediate surface of the pile since there will be some alteration in the moisture content after any exposure, however short. It can be proved fairly conclusively that if the moisture sample be taken after the first crushing on material the size of which is fairly uniform, the moisture thus determined will be from one-tenth to one-fourteenth lower than it should be, depending on the season of the year. Thus in ordinary summer weather, if a value of 5 per cent is obtained for the moisture, the true moisture is probably close to 5.5 per cent.

In taking a sample for laboratory purposes, it is rare that all of any material is either put through a sampling mill or hand sampled in its entirety. A certain proportion is ordinarily withdrawn at once and put through the sampling process. This is primarily a matter of sampling cost but may have important commercial considerations also. For instance, in sampling ore for smelting it is usually desirable to keep it as coarse as possible. On the other hand, ore to be milled can be crushed *in toto* previous to sampling. In sampling crystallized chemicals, it is usually undesirable to crush too finely. To determine this point, the sampler should know what is to be done with the material, but it is preferable to take the selection of the material which enters the sample away from the judgment of the sampler, so that machine sampling is best. It is at least imperative to take every fifth or tenth or twentieth shovelful rather than to allow a sampler to take a shovelful whenever his inclinations so move him, though Brunton says that at best the process is that of "shovel selection" rather than "shovel sampling." The man who is doing the work should also be watched to see that he takes shovelfuls of about the same size, both of the material accepted for the sample and of that going into the reject, and here the working period comes in, for at the close of a long period of shoveling, the shovelfuls will usually be much smaller than at the start.

Other plans than taking shovelfuls at stated intervals are necessary where material is not being unloaded by hand, but in any case the principle remains that the selection of the sample should not be left to the caprice of the sampler—thus the United States Steel Corporation in sampling ore arriving in hopper bottom cars specifies that a network of cords shall be stretched over the top of the car and that equal quantities of material shall be taken from under each of the points of intersection in the net.[1] In sampling certain homogeneous manganese ore arriving by steamer it is perfectly proper to take every twentieth or even fortieth scoop as it comes up through the hatch. The sample scoops are then unloaded into a car by themselves and that car alone later goes to a sampling mill.

[1] The full paper on the methods of the Steel Corporation for sampling ore in bulk was published in the *Jour Ind and Eng Chem*, 1909, p. 107, and should be referred to by anyone interested in this subject

It is also possible to take samples direct from the faces of ore in a vessel which is being unloaded, but this method is not ordinarily to be recommended, as it leaves too much to the judgment of the individual samplers

Of course these fractional-selection methods introduce hand sampling, and the more that can be eliminated, the better off we are. While the advocates of hand sampling claim that with a trained gang of men the actions are practically mechanical, this is untrue, for if they are trained they know what they are doing and why they are doing it, which virtually is allowing the ore to be handled by interested parties. In such cases it is either impossible for any man to submerge completely what he considers are his employer's interests, or else he consciously stands so straight as to lean over backward. The greatest errors introduced by hand sampling are: (1) In fractional shoveling, the shovelful is ordinarily not uniform, the ordinary tendency being to make the sample shovelful the smallest. The size of the shovelfuls will also vary through the day, as already mentioned. Moreover the place from which the sample is taken is at the discretion of the workman. (2) In coning, the larger pieces of ore invariably fall to the outside of the pile while the top retains the fines. Then when the pile is spread out the fines go to the very outside. As the moisture sample is ordinarily taken from near the surface of the pile and at this stage of the work and the fines contain the more moisture, this operates in favor of the buyer. (The process of "coning" is explained below.)

Cutting Down Samples.—Having obtained the original sample it is then subject to alternate reduction in size of the individual pieces and in the amount of the sample itself. Those cases are almost negligible where there should be two successive reductions in amount of the sample without an intermediate reduction in the size of the largest pieces making it up. It is not always necessary to crush the entire sample. Much time and expense can often be saved by screening a sample and crushing only the coarse portions, mixing them when crushed with the finer pieces which have bypassed the crushers. (The question of coarse pieces which will not crush will be discussed later under the heading of "Metallics," p. 581.) It is self evident that after this process pains must be taken to mix the portions thoroughly.

Reduction of the bulk of the sample itself may be done either mechanically or by hand or by a combination of the two. The hand operation is ordinarily known as coning and quartering. The material is piled first into a cone and then the top of the cone raked out so as to form the frustum of a cone.[1] Diameters are drawn across this at right angles and the opposite quarters are rejected. The remaining quarters are then again shoveled into a cone being careful that shovelfuls are taken alternately from the two quarters to go into the new cone. This cone is again flattened out and the quartering process repeated.

The two great dangers in this process are the tendency of large lumps to segregate at the bottom and outside of the cone, and unless great care is taken to place the shovelfuls exactly on the apex of the heap there will be an undue concentration of coarse material in some one quarter of the pile. The other is that in conducting the quartering operations the workmen will either invariably take or reject all of the large lumps which lie along the border line of the cut, thus causing the sample to contain an undue amount of either coarse or fine. In raking out the cone into a frustum the radial distribution of the material should not be disturbed. This question will be referred to again under "salting," p. 583, in discussing the operation known as "draw-

[1] A detailed description of this process is given by Jesse E. Stobbly, *Met. and Chem. Eng.*, February, 1913

ing the center." Care must be taken not to lose dust from the material and it may be necessary to sprinkle the pile from time to time in order to avoid this.

A piece of apparatus used in cutting down samples by hand work is the assayer's shovel, shown in the illustration. This consists in a number of parallel troughs

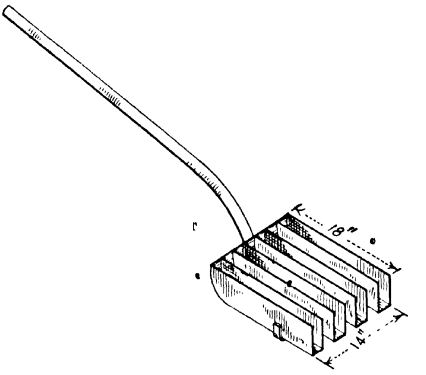


FIG. 1.—Split shovel

attached to a shovel handle, and separated by spaces of width equal to that of the troughs. When crushed ore is shoveled on to this shovel, a portion is retained in the trough and a portion falls through, thereby splitting the sample.

A variation of this idea is found in the Jones sampler which consists of a number of parallel triangular troughs facing in alternate directions (see illustration). One-half

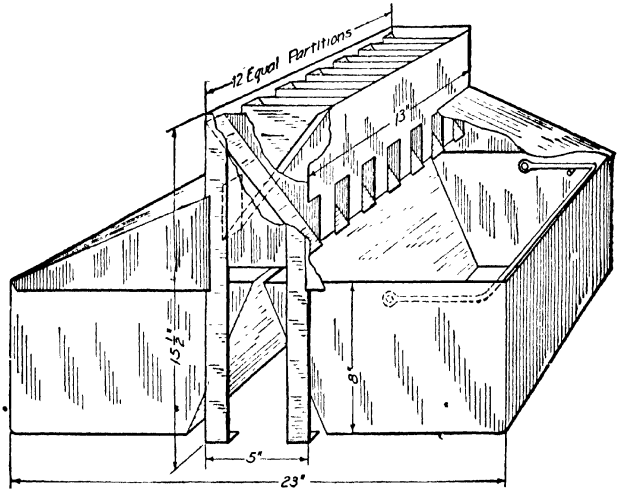


FIG. 2.—Jones sampler.

of the material must go one way and one-half the other. For cutting down very small and finely ground samples still another modification is the assayer's riffle, also shown in the illustration.

The mechanical samplers as ordinarily found are either the Vezin, Bridgman or the Brunton type[1] or some modification of them. In any case the sampling principle is to cut across a falling stream of ore, taking either successive portions of the stream as the sampler cuts across it or else diverting the entire falling

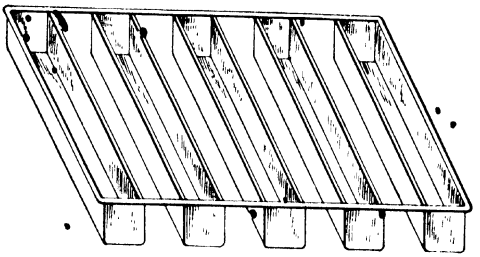


FIG. 3.—Assayers riffle

stream for a certain period into the sample. In either case the danger is the same, that the apparatus used should not be sufficiently large for the component parts of the ore stream; that is, the large lumps of ore are driven into the large

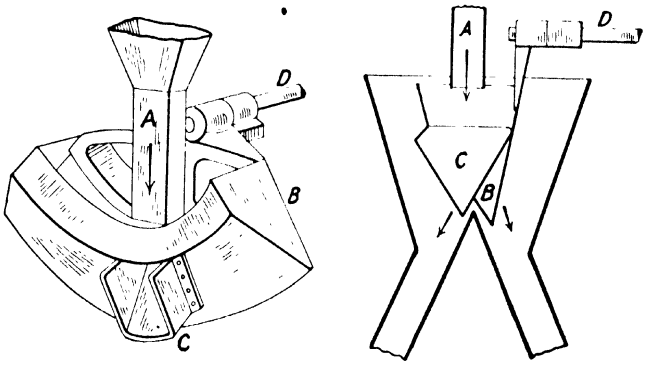


FIG. 4.—Brunton sampler

rejected portion leaving an undue proportion of fines in the sample. This is a matter which should be carefully watched, as should also be the point that the entire falling stream is diverted or is cut across and not merely a portion of it, for such a stream tends to classify itself as it falls, and a sample cut from one edge only will not be the same as one cut from the center, nor will the edges themselves ordinarily be alike. In rotating samplers it is therefore important that the cutting edges are radial planes.

The matter of relative size of piece and size of opening is illustrated very well by the sampler's shovel and the assayer's riffle. It is easy to see that these pieces of apparatus are entirely unreliable on material containing individual pieces of larger diameter than the width of the openings, for then these larger pieces will all be retained

[1] The original BRUNTON apparatus is described in *Trans* A. I. M. E., Vol. **13**, p. 639.

on the shovel or riffle. It does not seem safe to use these two pieces of apparatus with material the maximum pieces of which exceed one-fifth the width of the opening, and it seems probable that the same proportion would be a good one to apply to sizes of the lumps and cutout holes in machine sampling.

The Brunton sampler consists either in a wedge-shaped deflector plate that can be thrown back and forth in such manner as to send all the ore stream to a storage bin or to the sample, or in a scythe-shaped casting which swings back and forth in the ore steam. The drive is ordinarily by a connecting rod driven from a belted wheel, and by altering the position of the connecting rod the arc of travel is altered.

In the latter form most of the surface slants toward the storage-bin hopper, the remainder toward the sample bin and the stream of ore is directed according to which portion of the casting it is hitting. The proportion of ore deflected is altered by adjust-

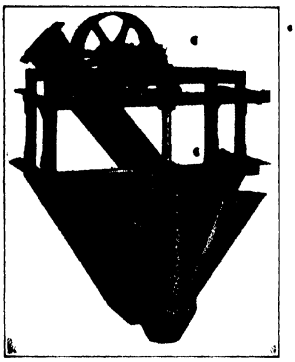


FIG. 5.—Vezin sampler.

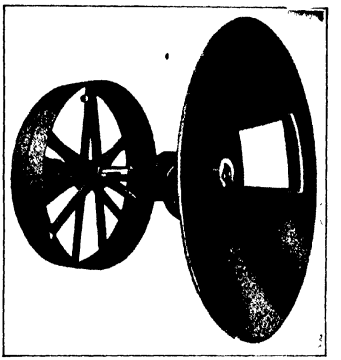


FIG. 6.—Snyder automatic ore sampler.

ing the arc of travel of the casting. As the arc is cut down, the portion inclined toward the sample bin constitutes a greater and greater portion of the part of the casting in use. In the former type of apparatus, the wedge, the adjustment is made by cams which may be set at varying angles. The sampler points one way during one part of the revolution and in the other during the remainder, so that any adjustment is possible.

Practically the same end as that attained by the oscillation of the Brunton sampler is gained by rotation in the Snyder sampler (this is not the Charles Snyder sampler spoken of on p. 571). This sampler consists merely of a circular casting shaped much like a miner's gold pan, having one or more openings (according to per cent sample desired) in its sloping flange, mounted on the end of a horizontal shaft provided with tight and loose driving pulleys.

In operation the sampler revolves 10 to 30 times per minute, the speed depending upon the size of the sampler itself and the size of the material being handled. The material to be sampled is directed by a spout so as to fall inside of the sloping flange of the sampler. The rejections slide off the flange into a receiving hopper. The sample drops through the opening in the flange as the opening passes under the spout. It is a most simple machine, and its only disadvantage is that the percentage of sample to reject is fixed by the ratio of the arc of the opening to the full circumference or 360°.

The Vezin sampler is shown in the cut, and as will be seen consists in a rotating cylinder bearing two or more scoops, which as they revolve, cut through a falling stream of ore, delivering the portion they cut out (the sample) through the truncated cone at the bottom, while the reject passes on the ore bin. Theoretically this sampler,

as well as the Charles Snyder[1] and Bridgman[2] types have the objection that centrifugal action disturbs the selection. In addition they are occasionally found made so that the edges of the cutting scoop are not radial, which gives improper selection, and unless they are rugged construction the edges of the scoops become bent, leading to improper results. These machines are often made so that several reductions in bulk of the sample are made without any intermediate crushing. This, I believe, is absolutely wrong. On the other hand, they have great capacity, require little headroom and are easily cleaned, with a hose, if necessary.

Crushing for sampling may be done in any apparatus that fulfills the following conditions: It must be easy to clean; it must not wear greatly, otherwise the material from the crusher will contaminate the sample; the material must not fly about, but must all be delivered at one spot. Hence, gyratory crushers, jaw crushers and rolls, are used for sample breaking, and ball mills, drug mills, small breakers and small rolls for final crushing. The three above conditions are the only essentials.

For feeding material to the crushing or to the conveying machinery, it should be remembered that shaking belts or tables all classify the material fed and hence tend to inaccuracy unless pains be taken to offset this tendency.

Coal Sampling.—Probably coal sampling is subject to greater proportional errors than is any other common sampling operation. This is not alone due to the fact that it is a cheap substance which means that not much can be spent upon sampling it, but is also owing to its deceptive appearance. The various parts of a heap of coal look beautifully homogeneous; it usually comes already partly crushed, but the point remains that the assumption of uniformity leads to bad errors. One swallow will come nearer making a summer, than will one lump of coal, picked out by the master mechanic, to making a good sample.

While the final preparation is a matter of ordinary coning, quartering and breaking down, the following, by C. E. Scott, is a good description of what ought to be done in taking the sample.

"The size of the sample shall not be less than the proportion of one part per 1,000, and the minimum size of any one sample shall be 100 lb; the maximum number of tons one sample shall represent shall be 1,000, and preferably much smaller than this, say, 250 tons. All the impurities, such as slate and pyrites, should be broken down in the original sample, and if this is done as each shovelful is taken, it will make the work much easier. In collecting the original sample from a railroad car it should be taken as the coal is being discharged; where the coal is delivered to the point of sampling in wagons, one large shovelful should be taken from each wagon; where it is delivered in a barge, the sample should be taken as the barge is discharging (if the discharging is accomplished by the aid of a bucket or belt convevor it is advisable to take advantage of this and obtain a small shovelful from the buckets or off the belt at regular intervals); where the sampling must be taken from a pile, a shovelful should be taken from all accessible parts of the pile, and the shovel should be filled from the coal underneath the surface. As the coal is collected it must be placed in a box, barrel, or can, of sufficient size, which has been thoroughly cleaned out before using. A lid should be kept on the container at all times to prevent dust, ashes, etc., from collecting on the sample. When the total sample is completed it should be put through a crusher or dumped on to a clean wood or cement floor, or on a canvas cloth, and crushed down

[1] *Trans.* A I M E, Vol **40**, p 570
[2] *Trans.* A I M E, Vol **20**, p 416

by means of a hammer until no pieces larger than 1 in. remain. The sample should then be mixed by shoveling it over itself into a conical pile."

Size-weight Ratio.—Many attempts have been made to deduce a proper ratio between the size of the largest pieces in the lot of material to be sampled and the size of the sample. Probably one of the best of these was a paper on "Accuracy in Sampling Coal."[1] This was an investigation into the cause of inaccuracies in sampling, based on both laboratory experiment and theoretical calculation. While the investigation was concerned with coal, the general results and reasoning are applicable to all substances:

SIZE OF SLATE CONTAINED IN COAL, AND SIZE OF ORIGINAL SAMPLE REQUIRED TO INSURE THE ERROR OF SAMPLING BEING LESS THAN 1 PER CENT

Size of slate, inches	Weight of largest piece of slate, pounds	Original sample should weigh, pounds
4	6 7	39,000
3	2 5	12,500
2	0 75	3,800
1½	0 38	1,900
1¼	0 24	1,200
1	0 12	600
¾	0 046	230
½	0 018	90

SIZE TO WHICH SLATE AND COAL SHOULD BE BROKEN BEFORE QUARTERING SAMPLES OF VARIOUS WEIGHTS

Weight of sample to be divided, pounds	Should be broken to, inches	Weight of sample to be divided, pounds	Should be broken to, inches
7,500	2	40	2 mesh
3,800	1½	5	4 mesh
1,200	1	½	8 mesh
460	¾	¼	10 mesh
180	½		

LIMIT BEYOND WHICH SAMPLES SHOULD NOT BE DIVIDED WHEN CRUSHED TO DIFFERENT SIZES IN LABORATORY

Size of coal mesh	Should not be divided to less than, grams
2	8,300
4	1,100
8	120 } Should be pulverized
10	55 } to at least
20	3 } 60 mesh

[1] E. G. Bailey, *Jour. Ind. Eng Chem.*, 1909, p. 161.

In order to obtain a sample which shall correctly represent any material it is necessary to crush to such a fineness that a particle more or less of any component of the material taken into the sample shall not materially affect its analysis or its value. The maximum error is determined by the ratio of the weight of the largest particle of metal or high grade mineral or impurity to the weight of the entire lot. The chance of finding a full-size piece of highest grade material would be much greater in a lot of ore crushed to 0.25-in. cubes than in a lot crushed to 1-in. cubes Therefore accuracy demands that the ratio between the weight of the largest particle and the entire lot shall increase directly as the fineness.

As a consequence of these considerations, in gold ore sampling it is customary to go a little beyond the above figures, both in size of sample and in fineness of crushing, while in sampling chemicals and other more uniform products, the samples may be smaller in weight. Tables for ore sampling follow:

WEIGHTS TO BE TAKEN IN SAMPLING ORE[1]

Weights		Diameters of largest particle					
Grams	Pounds	Very low grade of uniform ores, millimeters	Low grade ores, millimeters	Medium ores		Rich ores, millimeters	Rich and spotty ores, millimeters
				Millimeters	Millimeters		
.....	20,000 0	207 0	114 0	76 2	50 8	31 6	5 4
.....	10,000 0	147 0	80 3	53 9	35 9	22 4	3 8
.....	5,000 0	104 0	56 8	38 1	25 4	15 8	2.7
.....	2,000.0	65 6	35 9	24 1	16 1	10 0	1 7
.....	1,000.0	46 4	25 4	17 0	11 4	7 1	1.2
.....	500 0	32 8	18 0	12 0	8 0	5 0	0 85
.....	200 0	20 7	11 4	7 6	5 1	3 2	0 54
.....	100 0	14 7	8 0	5 4	3 6	2 2	0 38
.....	50 0	10 4	5 7	3 8	2 5	1 6	0 27
.....	20 0	6 6	3 6	2 4	1 6	1 0	0 17
.....	10 0	4 6	2 5	1 7	1 1	0 71	0 12
.....	5 0	3 3	1 8	1 2	0 80	0 50	
.....	2.0	2 1	1 1	0 76	0 51	0 32	
.....	1.0	1 5	0 80	0 54	0 36	0 22	
.....	0 5	1 0	0 57	0 38	0.25	0 16	
90.0	0.2	0 66	0 36	0 24	0 16	0 10	
45.0	0 1	0 46	0.25	0 17	0 11		
22.5	0.05	0 33	0 18	0 12			
9.0	0.02	0 21	0.11				
4.5	0.01	0 15					
2.25	0.005	0 10					

[1] RICHARDS "Ore Dressing," Vol 2.

SIZE-WEIGHT RATIO IN SAMPLING[1]

Diameter of largest particle, inches	Minimum weight of sample, pounds, Colorado practice
0 04	0 0625
0 08	0 50
0 16	4.00
0 32	32 00
0 64	256 00
1 25	2,048.00
2 50	16,384.00

SMALLEST PERMISSIBLE WEIGHT FOR SAMPLES OF A GIVEN SIZE[2]

Size, inches cube or mesh	Weight of sample, pounds	Ratio of weight of largest cube to weight of sample	Effect on value created by one cube assaying $100,000 per ton, of sp. gr. 5
2	10,000	1: 7,000	$14 42
1½	5,000	1: 8,300	12 17
1	2,000	1: 11,000	9 00
¾	1,000	1: 13,000	7 50
½	400	1: 18,000	5 62
⅜	300	1: 31,000	3 17
¼	200	1: 71,000	1 40
3/16	100	1: 83,000	1 20
⅛	75	1: 220,000	0.44
6 mesh	50	1: 430,000	0 23
10 mesh	25	1: 930,000	0.107
18 mesh	10	1:1,900,000	0.051
30 mesh	4	1:4,200,000	0.023
50 mesh	1	1:5,500,000	0.018

SCHEME FOR SAMPLING RICH ORES WITH VEZIN SAMPLERS[3]

	Inches	Sample, per cent	Pounds in 100 tons
Maximum size of cubes	1 00	20 0000	40,000
Maximum size of cubes	0.25	1.2500	2,500
6 mesh	0 0625	0.0785	157
30 mesh	0 0171	0.0050	10

[1] E. A. SMITH: "Sampling and Assay of the Precious Metals."
[2] R. H. RICHARDS: "Ore Dressing," Vol 3.
[3] R. H. RICHARDS: "Ore Dressing," Vol. 3.

Many experiments on the sampling of gold ores lead to the belief that carrying the grinding beyond 100-mesh does not add to the accuracy of the sampling, and that at this fineness equally good results will be obtained whether the material to be taken for the assay be cut out of the sample by one cut of the spatula or taken by various cuts from over the entire surface of the sample.[1]

We may, I think, therefore take that 100-mesh is as fine as it is necessary to reduce any samples whatever, so far as accuracy of sampling is concerned. On the other hand, since I have seen more concordant results obtained on a 60-mesh sample after reducing it to 80-mesh, we may conclude that 80- and 100-mesh mark the limits of desirable sampling. This totally ignores the question as to what are the best limits for manipulation from the chemist's and assayer's side. It may safely be assumed that no material requires finer grinding than does a spotty gold ore.

It is also of importance to note that contamination of the sample with material abraded from the grinding machinery increases rapidly as the mesh of the sample is cut down, so that this in itself offers a reason for keeping the mesh size as large as possible.

The contamination of samples of those materials which can be easily crushed by particles of the sampling tools, reference to which has previously been made, may reach greater proportions than is ordinarily credited. In sampling coke using a Braun pulverizer I have shown that the amount of iron introduced in the final sample may equal 1 per cent of its entire weight, all of which will of course show as ash when that constituent is determined, meaning that this determination will be at least 6 per cent from the true result and may be as high as 20 per cent. From the ordinary bucking board and muller used for ore crushing by a not over-industrious Mexican I have seen iron to the extent of 3 per cent of the weight of the sample introduced into it. Of course if the sample is to be assayed for copper, lead, silver or gold, the introduction of iron in this way saves a considerable amount of money in the course of a year in payments for these valuable metals, but the inaccuracies introduced are fatal to good furnace practice, even if one has chloroformed his conscience.[2] For this reason the selection of material for the grinding tools to be used in sampling is a most important question. Chrome steel and manganese steel should be used to replace cast iron which is usually used, and incidentally, the greater wear obtained from these harder substances will almost more than pay for the difference in original prices. For this reason too bucking boards and mullers which have been cast with chilled surfaces should be watched and when the chilled surface is worn through they should be promptly discarded.

That iron can be introduced to the extent of 1 per cent of the weight of the coke sample may possibly be questioned. However, there is no doubt that in the samples spoken of this amount of iron was present in a metallic state as was determined by agitating the sample with a neutral copper-sulphate solution, washing the resulting mass free from the resultant copper and iron salts and determining the metallic copper left precipitated on the coke dust. This iron equivalent of this amount of copper was then calculated. The metallic iron thus shown to be present was not iron reduced from the ashy constituents of the coke by the action of the incandescent carbon

[1] LEWIS V. WRIGHT: *Min. Mag.*, November, 1910.

[2] The introduction of metallic iron into the sample also results in the assayer's finding a heavy black residue when the sample is panned that not infrequently results in all hands starting to look for iridium. It also prohibits the use of evolution methods for the determination of CO_2 in the ore.

during the coking process for when the same coke was ground in Abbé mills or crushed in porcelain and agate mortars using porcelain and agate pestles the sample thus produced did not react with neutral copper-sulphate solution, nor was the analysis of the ash obtained by burning off the coke at all the same, as the latter case showed much more silica and much less iron. Reference to this subject of sample contamination will be made again under copper-bullion sampling.

SAMPLING METALLIC MATERIALS

In sampling metals there are two main dangers to be guarded against. First, that the outside of the bar or slab will ordinarily have a certain amount of dirt on it of character entirely dissimilar from the inside of the bar and also that even in the interior of the bar the metal is as a rule not homogeneous. In fact it is the rarest exception when an alloy of two or more metals does not segregate upon cooling. For instance, in a copper bar which averages 120 oz. of silver to the ton individual samples can be drilled from it which will run anywhere from 80 to 200 oz.

As regards dirt and scale on the outside of the bar there are times that a portion of this belongs in the sample. This will be the case in sampling copper or lead bullion where the metal is to be paid for upon assay. As the dirt is weighed with the shipment a certain portion of it should appear in the sample. On the other hand in handling bars of bullion of any sort it is a very easy matter to detach more of this dirt or scale and get it into the sample pan than should properly be there. Here then is a case in which the judgement of the representatives of buyer and seller must be used as to when the proper amount of dirt is getting into the sample and when this is being exceeded.

The fact that there is dirt and scale on the outside of metallic bars gives rise to some very curious consequences. It would appear at first sight that in the drilling of copper bullion it would make no difference whether the drill was pushed through the bar from top to bottom or *vice versa*, yet this is not the case, nor is it by any means merely a theoretical difference. The gold and silver contents may be affected by more than a per cent of their value and the copper content itself sensibly modified by the direction in which the drilling is done. This is due not alone to the fact that ordinarily the top of the copper bar will have more dirt and scale on it than will the lower surface, but also to the fact that the interstices in the metal will retain some of the fine powder first drilled off when the metal is being drilled top up, while all of this dirt will fall into the sample when the bar is being drilled bottom up.[1] In the sampling of lead bars a punch is ordinarily used so that this question of dirt does not enter in any great degree. On the other hand the punch is ordinarily driven half way through the bar so that it is important in order to avoid the effect of segregation that the available length of the punch should not be greater than half the thickness of the bar. For if it is, it results in an undue amount being taken representative of the center of the bar as compared with that representative of the outside. In punching lead bars it is sometimes the practice of the sampler to wet the punches with oil. As the punchings are later melted down and small sample bars cast from them, this results in inaccuracies for the oil will reduce the oxide of lead present and give a higher assay than should be obtained. On the other hand if the samples are allowed to remain uncovered too long before melting the oil causes any flying dirt to stick to the punch cores and the sample will be contaminated in this way.

[1] *Eng and Min Jour*, Nov 5, 1910, p. 897.

The melting is ordinarily done in a graphite crucible. Of course this in itself tends to a certain reduction of lead oxide but probably not more than sufficient to overcome the effect of the oxygen of the air. This latter reagent makes it necessary that this melting should be done as quickly as possibly and at the lowest temperature at which the molten lead will be completely fluid, for if the temperature be too high or the mass be kept too long in molten state the lead will scorify, resulting in the sample being higher in gold and silver than the bars actually are.

It should be unnecessary to point out that when wooden blocks are used under material that is being drilled, care should be taken not to drill into these blocks, but too many samples are found containing wood chips to allow this caution to be omitted.

Samples of gold and silver are ordinarily poured from the molten metal and consequently there is but little danger of contamination by particles of the sampling tools. Lead is so soft that it also is not affected. With copper, iron, steel and some other metals the sample is invariably contaminated with particles from the sampling tools. Thus in copper drillings which have been ground the contamination may amount to as much as 0.4 of 1 per cent. It might appear that in this case it would be comparatively easy to pass the drillings over a magnet and remove all of this extraneous material. Unfortunately if this were done an error would be introduced on the other side because blister copper will have a certain amount of converter slag adhering to it some of which will enter the sample, where it properly belongs.[1] This slag is, like iron, paramagnetic and will be removed by a magnet. In sampling steel or iron the case is even worse. The only accurate method is to use sampling tools of a hardness greatly in excess of that of the metal to be sampled and if possible to ascertain the loss experienced by the tools as compared with the total weight of the sample using these weights and the analysis of the tools and of the sample as the basis for the correction. Of course such refinement as this is happily seldom necessary.

It will occasionally happen that metallic material will be so dirty from adherent slag, matte or other foreign material that it is necessary to melt the entire shipment down, recast it and sample both metal and scoria separately (see paragraph on "Metallics," p. 581).

Owing to the fact, already referred to, that molten metals segregate on cooling, drillings from any one portion of the bar will ordinarily not be representative of that bar. There is of course a point in going from center to periphery of a bar where the sample will be representative of one or more elements, but not necessarily of all. That is, in a lead-silver alloy the silver content will be at a maximum at the surface of the bar and a minimum at the center, while the lead will be at its minimum at the surface of the bar and its maximum at the center. While there will be some intermediate locus at which the content of either silver or of lead represents the average of one of these materials in the bar, whether these loci will be identical depends on the other elements present.

As a consequence a sample must be taken which will represent all portions of the bar. In copper this is obtained by drilling holes in successive bars by means of a templet which covers all, one-half, or quarter of the bar (my own preference being for the last).[2] The templet is so arranged that it spaces holes evenly over all, one-half,

[1] *Eng. and Min Jour* Oct 15, 1910, p 752

[2] Theoretically the quarters are identical, and it takes fewer holes to cover a quarter templet than a whole templet, spacing the holes on 1½ in squares. Consequently in lots of bullion where the number of the bars are not integral multiples of the number of templet holes, a better distribution of holes can usually be attained with quarter templets than with whole, as there will, on the doctrine of chances, ordinarily be fewer holes to scatter, after the even rounds have been drilled.

or one-quarter of the bar and not over 1½ in. apart. While the more durable templets are built of sheet iron, the best material, all things considered, is wood. Flanges, as shown in the illustration of the templet, catch both edges of the pig or bar and serve to fix the location of the hole. In the templet that is here illustrated, chalk is rubbed on the surface of the templet over and around the desired hole and some of it falls through the hole into the bar. This spot is then marked with a punch, the dust brushed off the bar and drilling done by the punch mark. (With a sheet iron templet, the punch is occasionally driven through the templet hole and no chalk used. The drill holes must go completely through the bar and half the drilling should be done from the top and half from the bottom. With lead, as a rule, the punchings are taken on successive bars so that each hole is one-fifth the width of the bar further over and

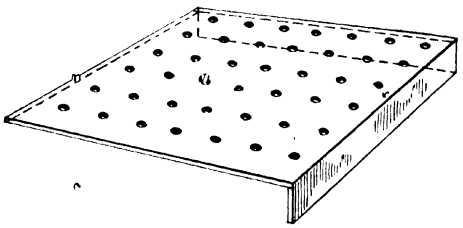


FIG. 7.

one-fifth further along the length of the bar than was the preceding one. If a single pig of iron is being sampled the sample should be obtained either over the whole surface of the pig or by drillings taken from several points scattered over the entire surface. In samples of gold and silver bars if they are not taken from a poured sample the cuttings from the bar should be taken from both top and bottom.

Ladle samples taken by abstracting a ladleful of molten metal from the charge and granulating it in the water are often recommended but the matter of segregation applies to them likewise. No sooner does metal begin to chill in a ladle than segregation begins to take place and if any skull forms inside a ladle it will ordinarily differ markedly from the material poured out. For this reason the ladle used in sampling any metal should be hot as compared with the metal to be poured from it. The sample should be poured quickly and no more should be poured after a skull has begun to form in the ladle.

Lead Sampling.—As can be seen from the character of the metal, lead can be sampled with less likelihood of error than can any other metal. The process is thus described by Raht.[1]

After melting the bullion bars down in a kettle holding about 20 tons, the coppery dross is skimmed off and sent back to the blast furnace to be smelted over; with this one of the worst sources of error in sampling is removed. The bullion is then thoroughly stirred, say, for 5 min., and while this is still going on a number of samples are taken by means of a small ladle holding approximately one-half an assay ton of metal. It is important that this ladle should be at least as hot as the bullion, so that none of the metal would stick to its surface, otherwise the samples would be too low in silver. The samples thus obtained are taken direct for assaying without any trimming or clipping. Instead of trimming the sample down to the exact weight of half an assay ton, the exact weight of each sample is ascertained, whatever it may be, and from

[1] RAHT, A: The distribution of silver in lead bullion, and the different methods of sampling. *Min. Ind.*, Vol. 3, 1894, p. 414.

the resulting silver button the contents are figured. Care is taken, however, in the selection of the samples for assaying out of the great number originally taken that these should be somewhere near the same weight, so that when they are cupeled side by side they would finish about the same time.

It will be seen that all the objections to punch sampling are met in this method. Still, another one might be raised against it, which is the uncertainty whether the mixture was thorough. I must say that this does not appear to carry much weight, but it can be overcome by taking samples at regular intervals out of the stream of metal running from the kettle into the molds. These samples would have to be remelted in a graphite crucible and out of this again one-half assay-ton samples taken, which are then treated as above. This method, of course, brings in again the objection to the remelting. There cannot be the least doubt that either of these two dip samples would be nearly absolutely correct, but they can be carried on only at the works of the seller of the bullion, as it would be next to impossible to obtain a correct sample from the dross skimmings. It is to be hoped that the dip sample will be generally introduced wherever practicable, and so do away with the annoying sample and assay differences between the bullion producer and refiner.

SAMPLING PIG IRON

In the sampling of pig iron one of the optional methods of the United States Steel Corporation is described as follows by the chemists' committee of that corporation:[1]

Plate or Pat Test —With a suitable hand ladle a portion is dipped from the stream of molten iron and, with the spoon of the ladle resting upon a clean, dry, iron plate, a pat of such size as may be desired is poured thereon

The use of the water-shot sample is to be considered as in violation of the standard method.

Number of Samples to be Taken —As tending to a reasonable degree of accuracy, it is recommended that a portion be secured, timed as nearly as may be practicable for the middle of each ladle of iron representing the cast. Equal portions from each of these samples are conveniently combined for subsequent analysis.

Preparation of the Sample —The tests are either drilled or crushed, as required. If crushed, only that portion passing an 80-mesh sieve is used for the subsequent analysis.

In view of the segregation that takes place in any ladle, as has been commented on, and in view of the differences that exist between the coarse and fines of cast iron, the above may do for furnace control work, but for accurate sampling it is a capital set of instructions on how not to do it.

Shot samples may be taken from a charge which is being poured by batting through the falling stream of metal so that the resulting shot goes into a nearby pan of water.

Moisture in Bullion.—In metals which are not completely solid and which have been cooled under water, moisture is possible and this moisture is not driven out even at 212°. This is of commercial importance in pig copper which has been bosh cooled. Apparently the explanation is that the water gets into minute holes in the metal, the necks of which close completely due to the contraction and distortion on cooling and will not reopen when the material is heated to 212° only.

[1] The methods of the United States Steel Corporation for commercial sampling and analysis of pig iron, *Jour. Ind. and Eng. Chem.*, Vol 4, 1912, p 801.

As I have shown this moisture may amount to as much as 0.6 of 1 per cent and is not completely expelled at temperatures below 240°F.[1]

In sampling pig iron it is ordinarily the grade of the pure pig which we are concerned with and not the average analysis as affected by adhering scale and sand. For this reason in taking a sample of pig iron either by drilling or filing from the broken end of a bar it will be found of great assistance to wrap a strip of paper tightly around the bar several times, thus preventing any scale or sand from dropping off into the sample.

In sampling refined copper bars, which are probably as nearly homogeneous as any commercial metal, most of the analyses can be made from borings taken anywhere except just at the surface of the bar. For suboxide determination filings or sawings are best. Teh Cananea Consolidated Copper Co. formerly ran a set of six small parallel power-driven saws for the preparation of such samples. These samples must be freed from iron by means of a magnet and since the original material is free from iron and iron oxides, no error is thereby introduced.

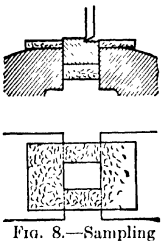


FIG. 8.—Sampling pig iron.

Where the sample must be taken from an iron or steel surface by planing, it is well to hammer off all scale, sand or other extraneous material from the outside of the bar and then set up the bar so that it projects up through a sheet of stiff paper as shown in the illustration. The shavings will then be caught on this paper and can easily be transferred to a sample bottle. Care must be taken not to run the planer too fast, for if this precaution be not observed the coarse shavings will fly away and be lost, leaving only fines behind, which seriously vitiates the sample.

In general there is a great difference between the coarse and fine portions of any sample. With iron any free carbon in the metal pulverizes readily and is found in the fines. How great the difference between the coarse and fine is shown by the following analyses of dark gray cast iron planings screened through an 80-mesh sieve:[2]

	Coarse, 173 g., per cent	Fine, 16 g., per cent	Calculated composition, per cent
Total carbon	2.62	11.66	3 39
Graphite...	2 38	10 91	3.10
Combined carbon	0 24	0 75	0.29
Silicon.....	2.44	2.27	2.42
Phosphorus	0.51	0.56	0.515
Sulphur..	0.08	0.073	0 079

Another case (taken from the same source) was a Swedish gray iron which was planed over the entire cross-section giving 693 g. of shavings. These were screened so as to obtain three portions: On 80-mesh; through 80-mesh and on 120-mesh; and through 120-mesh. Analysis of the screened portions gave results as follows:

[1] *Eng and Min Journ.*, Dec 3, 1910, p. 1095

[2] BAUER and DEISS: "Sampling and Analysis of Iron and Steel."

	Coarse, 469 g., per cent	Medium, 193 g., per cent	Fine, 31 g., per cent	Calculated analysis, per cent
Total carbon	3 53	4 04	22 00	4 50
Graphite...	2 12	2 53	20 94	3.07
Combined carbon	1 41	1 51	1.06	1.43
Silicon	0 81	0 83	0 76	0 80
Phosphorus.	0 051	0 044	0.03	0 048
Sulphur...	0 017	0 014	0 013	0 016

On a sample of comparatively clean converter copper, screened over a 12-mesh screen, the portion on the screen assayed 98.94 per cent Cu, that which passed the screen 97.21 per cent. The proportions were as 21:1.

There is no need of multiplying instances with analyses of other materials. The sampler as well as the analyst must realize the variations that may exist between the coarse and fines of a sample and the sampler must so arrange his methods that the correct proportions of each may be turned into the laboratory. As to how the analyst will treat the sample after it is delivered to him does not fall within the scope of this book.

Hardened steels may be annealed before machining. Annealing for 15 min. at 750 to 800°C., followed by slow cooling until the pearlite point is reached (700°C.) is sufficient to anneal carbon steels. Below 600°C. the steel may be cooled as quickly as desired. In the case of certain alloys and self-hardening steels it will be necessary to use chrome-tungsten and other alloy steels for the planing tool. With material that cannot be worked even with special steels, it is necessary to knock off small pieces from different parts of the sample and to pulverize these pieces. It is recommended by Deiss and Bauer that the sample be wrapped in heavy linen cloth before pulverizing with the remark that the broken pieces must be carefully cleaned to free them from linen fibers. It should be noted that in cases of this class that carbon analyses are always subject to some doubt, as it is next to impossible to remove all of the cloth.

As a very elementary precaution, in taking samples of iron or steel, it is well to look at the drills or other cutting tools, to see that no large pieces have been broken out of them. If there have been, these pieces can usually be found and taken out of the samples.

METALLICS

The limiting case of variation between coarse and fine material in the same sample is that of metallic particles or masses occurring in material which otherwise is capable of being crushed. In this case the sampler should weigh the metallic and non-metallic portions of the sample as soon as they can be properly separated, sample each separately and report the original weights to the laboratory.

There are often metallic substances occurring which can be ground by suitable means and the powder added to the pulp sample. This, however, is a questionable procedure, for this powder must be of different composition from the easily pulverized material and its introduction into the sample makes a "spotty" sample. Much of the trouble, for instance, with samples of gold ore that give discordant results is due to forcing through the sampling screen small metallic particles that should have been removed and weighed and reported as "metallics."

It may be noted at this point, that the formula for computing the average value of a sample containing metallics is as follows:

If W = weight of pulp
w = weight of metallics
A = assay of pulp
a = assay of metallics

Then average value V equals $\frac{WA + wa}{W + w}$

Occasionally, as in sampling reverberatory slags, metallics will be taken out at each stage of the crushing. In this case a note should be made of the relative weights of metallic and non-metallic portions at each stage, but it appears to involve no great error to turn in but one sample of metallics along with the final sample of pulp.

The assay of the "fine" of the next to the last stage must be calculated from the assays and weights of the coarse and fine of the last stage. The assay of the coarse of the next to last stage is assumed to be the same as the assay of the coarse of the last stage, and so on.

In the general sampling of slags and other fused products it should be noted that these materials will decompose most easily when they have been suddenly chilled, and it is, therefore, recommended, for the convenience of the analyst, that this be done when possible, in sampling fused masses.

SAMPLING OF LIQUIDS

Concerning the sampling of liquids or semi-liquid material there is not much to say except to point out the necessity of rapid agitation to insure uniformity of the bulk to be sampled and drawing off the sample during the agitation or so quickly thereafter that segregation has not had time to take place.

The same precautions are necessary in further laboratory tests of these samples. Even though the liquids contain no sediment it must still be remembered that temperature changes in the room in which a liquid is standing are sufficient to cause differences in concentration of dissolved solids between the top and the bottom layers.

Errors are sometimes introduced through samples being taken at high temperatures and crystallization occurring due to cooling down the samples before use is made of them.

As to the matter of the proper treatment of samples where there is a sediment; that is, how to estimate correctly the influence of the sediment on the original sample and to what extent the sediment should be washed and what is the influence of the washing water upon the sample, no general directions can be given.[1] This is a matter that must be determined by the chemist for each case independently. The general instruction can, however, be taken to heart that where these samples are not routine matters and the procedure absolutely worked out it will invariably pay to recheck these calculations after making them, or better still, to attempt to deduce the final result by an entirely new chain of reasoning.

SAMPLING GASES

In sampling gases it is again difficult to give general directions. The use of two bottles connected by a rubber tube attached to glass or metal tubes reaching

[1] The classic tables bearing on samples and problems involving a pulp suspended in a liquid are those of G. H. CLEVENGER, H. W. YOUNG and T. N. TURNER, *Eng. and Min. Jour.*, Dec. 19, 1914. Reference to this article should be made if many such samples are to be taken and assayed.

to the bottoms of the bottles and passing through two-hole corks, the other aperture being closed by another glass tube running into a rubber tube and stop cock, as an aspirating apparatus is well known. The apparatus is simple, but has the grave defect that the water over which the gas is usually collected absorbs the easily soluble gases, such as CO_2, NH_3, SO_2 and the like. This can be obviated to some extent by trying to saturate the water in the bottles with the gas to be collected but there still is danger either that the water will not be nearly enough saturated to stop absorption or that it will contain so much gas that it will be in unstable equilibrium and will be given off into the sample.

To a certain extent these errors can be avoided by the use of a 10 per cent sulphuric-acid solution, as the solubility of most gases (except bases) is less in this than it is in water. The errors can only be entirely done away with, however, by collection over mercury, or by the use of previously exhausted vacuum tubes, the valve of which can be opened in the gas to be sampled.

In sampling furnace gases the results are almost invariably vitiated by a rush of air along the sampling tube down into the zone to be sampled. Leaky joints in the apparatus should always be carefully watched for also.

INTENTIONAL VITIATION OF SAMPLES

Salting.—Of almost equal importance with knowing what one must do to obtain correct samples, is to know what may be intentionally done to render one's samples incorrect. This is, of course, of most importance to the mining engineer who is sampling mines, or to those engaged generally in sampling for the precious metals, but the sampler of any sort of material should know what may be done to render his work misleading.

Many of the following methods are taken from a paper by George A. James on the subject.[1]

Salting may, of course, be innocently or criminally done. Among the ways in which the latter may occur is the use of old coin bags for carrying samples in. The abraded particles left clinging to the bags may cause serious errors. Another way of salting one's own samples is to use one sack for two samples, separating them by a string around the center of the bag. In such a case the samples must be removed by cutting both ends of the sack, leaving the string tied. Inferior or porous sacks must be avoided, or else the fines may be lost through the meshes of the bag. Canvas used for catching the sample as broken in the mine may be contaminated, as may also the tools. This last remark applies with equal force to everything used throughout the sampling process. Proper allowance is not usually made for the pulp that may be retained by the grinding machinery, nor for metallics which may stick to the muller, bucking board, etc.

As a rule assayers do not give sufficient attention to drying the samples properly. While the failure to consider 2 to 3 per cent of water may at times be a wise factor of safety, omission of proper drying may sometimes lead to disastrous errors.

The use of the precaution commonly taken to overcome possible salting, washing the ore with water, is not so efficient as is usually supposed. While gold chloride and silver nitrate are both soluble, they are, after drying on the ore, usually reduced and rendered insoluble. Seals are of little value, as a whole wax seal can be raised with a knife, and later replaced intact. Cloth or paper bags yield to the hypodermic syringe while even glass bottles will succumb to a hypodermic needle thrust through the cork.

[1] *Min. and Eng. World*, May 20, 1912, p. 1099.

The best means of avoiding the effects of salting is to render its determination easy. This may be done by taking a few samples of utterly worthless waste rock in with one, and later mislabeling them, or better still, by roughly dividing a sample in a mine, and making the two portions of uneven weight. To salt such samples artistically enough to raise the values of the two portions equally, can usually not be done in the time and with the facilities at hand. Resampling is, of course, necessary when salting has been discovered.

Salting in precious metal samples may also be done by use of gold under the finger nails, or in the hair or beard, or by cigarette or pipe ashes carelessly (?) dropped into the sample.

A method of salting practically impossible to detect, or rather a method of influencing the sampling, is known as "drawing the center." In this the men who are piling up the cone purposely place the successive shovelfuls a little to one side of the apex (always moving the new apex in the same direction) Eventually this gives a pile with the original apex of the cone well to one side of the new and buried in the cone. The quarter containing the original apex will then contain an undue proportion of fine and if this quarter and its opposite are taken the sample contains too much fine; if the adjacent quarter and its opposite are rejected the sample contains too much coarse. These quarters will be either taken or rejected according to which way the sample is to be thrown. A way of avoiding this is to place a small stick upright in the center of the cone as soon as it is well started and seeing that the stick always is kept in the center of the heap.

In general, in watching any sampling by the coning and quartering methods it is advisable continually to compare the looks of the rejected heap with the accepted, and if it does not look right, repile the entire sample. In general it should be remembered that in coning non-homogeneous material there is no mixing takes place, but rather a classification, due to the large pieces rolling to the outside of the pile. Coning and quartering is not a means of mixing, it is only a means of dividing a sample.

Ore sampling may seem unduly emphasized in the above remarks, but when it is remembered how much money changes hands each year on samples of ore and of copper bullion it can be seen that this part of the subject deserves the space given to it.

Moreover, it is believed that the man who can take fair samples of ore and of bullion, and can avoid being stuck with unfair samples when some one else is doing the sampling, will be amply able to sample anything else that may be presented to him.

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SECTION XVII

FERMENTATION

By C. Glaser, Ph D[1]

Introduction.—While fermentation has been used since the days of barbarism by men to alter the composition of liquids containing certain organic substances, such as the juices of certain fruits, or artificial solutions extracted from grain, no one until recent times had any idea of what was really the cause of changes observed. Wine has been made for thousands of years and even beer has been brewed for many centuries, but it was only with the advent of the microscope that efforts to elucidate the mysteries became promising; and even then, the explanations offered were not substantiated by the facts, as developed less than 70 years ago by Pasteur and his co-laborers. Between the years 1854 and 1871 Pasteur devoted a large portion of his time to these researches and his theory, developed in opposition to the views held by other investigators (even a man like Liebig being in the opposing camp), and slowly accepted after this period, has stood the rigid tests of criticism.

It has been improved and enlarged upon since, by many investigators, but his leading conclusions are as true to-day as they were then and his theories have enabled mankind really to understand what is going on, when a sugar solution of medium concentration commences to show a few gas-bubbles after it has been exposed to the air, and in a few days goes over into an apparently boiling mass without much rise in temperature, only to fall back into quiescence after a further lapse of time

The gas given off had been found previously to consist mainly of carbon dioxide and the liquid, left behind, to contain alcohol A sediment, formed in the liquid, called "yeast" was known to be capable of starting fermentation again in fresh sugar-solutions and of repeating the cycle of actions above described

Pasteur's discoveries showed that certain organisms have a preference for certain optically active organic acids, in so far as they would, for instance, consume dextro-tartaric-acid, while they would not touch the levo-rotatory form He developed from this his theory of dis-symmetrical action of living microbes as a general principle. In his report to the Faculté de Science at Lille, France, he was soon able to report the systematic breaking down of potato-starch into sugar, alcohol (ether) and vinegar by the actions of certain microbes, thus extending the previous realm of fermentation processes. He also got a glimpse of the possibility of fermentation without living cells, but with an extract therefrom, which was a forerunner of Buchner's later discovery, (about 1896–1897) that the extract of yeast cells, carefully freed from the cells and constituting merely the liquid part thereof, would quickly decompose sugar in solutions into carbon dioxide and alcohol.

Fermentation a Catalytic Process.—This latest discovery enables us for the first time to give a concise and exact definition of fermentation, as a catalytic decomposition of sugar by zymase into alcohol and carbon dioxide, zymase being the enzyme extractable from yeast-cells. So far it has not been practicable to

[1] Consulting chemist and biologist, Baltimore, Md.

isolate in quantity this enzyme and the discovery of it, while clearing up the mystery of fermentation, has had no important practical results. We can state, however, that the appearance of secondary products such as acetic, lactic and butyric acids is due to impurities in the yeast in the shape of the bacteria corresponding to these products.

From the above researches, in which many other investigators were also active, it has become possible to lay down positive rules for the production of alcohol on an industrial scale from material either containing (1) fermentable sugar, or (2) compounds which can be converted by hydrolysis into fermentable sugars. To this latter class belong the "grains" (wheat, corn, rye, barley, rice, potatoes) with their considerable percentages of starch; also starch obtainable from other vegetable sources, and to these materials has lately been added wood in the shape of shavings, which can be partly hydrolyzed by dilute hydrochloric or sulphuric acid, acting at a high temperature under pressure on all polysaccharides present, even when in the shape of hemicelluloses and celluloses, but at a decreasing rate, as the last named increase.

To class (1) belong the sugar cane, the sugar beet, wine grapes and many other fruits. Sugar cane is the basic material for Jamaica rum; rice for arrac; while the sugar beet is raised in European countries and also in recent years in the Western States to a considerable degree for making the finer grades of alcohol. Potatoes as a source of alcohol were proposed as early as 1682, but only since 1820 have they been used for this purpose in large quantities, which however are lately reported to be falling off again. The processes of converting starches and other polysaccharides into fermentable sugar will be considered later in their most important modifications.

When we speak of "alcohol" we usually mean only the most important member of a large group of chemical substances, comprised under that name as a class, namely ethyl alcohol, which has the chemical formula C_2H_5OH and is also called "spirits of wine." It was prepared as early as the eighth century by distillation from wine, as described by Marcus Graecchus. However, only in 1796 was it first prepared free from water by Lowitz and by Richter.

THE PRODUCTS OF FERMENTATION

Enzymes and Ferments.—To the most important and interesting products of metabolism belong the enzymes or ferments. Since they are commonly ejected by the living cell, they are genuine "excreta." But since they play the most important part in the questions of nutrition of and addition of energy to the cell, they can not be compared with those elimination products which the cell discards because it has no further use for them. They must rather be considered as a tool with which the cells act upon their surroundings, in order to draw from them the greatest possible advantage.

The following important functions are fulfilled by the enzymes: (1) to change the character of the nutrious substrata in such a way that they are rendered fit for food; (2) to produce heat-energy by oxidations and exothermic decompositions, which are under the given relations a condition of life to certain microörganisms; or (3) they may exercise both these functions together. Many things point to the fact that enzymes participate in reductions and in syntheses. It may also be maintained that the same enzymes which produce exothermal decompositions, may under certain conditions carry on processes diametrically opposed, and that they are capable of rebuilding again by absorption of heat the molecules which they previously have decomposed.

So far we do not know what the enzymes are in a chemical sense. None of them except diastase has been prepared in a state of purity and their constitution is yet shrouded in mystery. We can only state that they are a part of certain living cells, from which they can be separated by rupturing the cells and pressing out their protoplasma. This latter substance is the ultimate carrier of the enzymes, as proven by Buchner's researches. Attempts to separate the enzyme from the cell-juice have not led to encouraging results, for all attempts to purify a primary precipitate by repeated precipitations with alcohol have led to a great weakening and finally complete disappearance from the product of its enzymatic powers. Pure enzymes are therefore not yet known. The actions of enzymes are greatly influenced by temperature and, as a rule, come to a stop only a few degrees above their respective optimum temperatures.

Invertase, an enzyme occurring in many saccharomycetes and bacteria splits the molecule of cane sugar by hydrolysis into two molecules of grape sugar.

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 \text{ (dextrose)} + C_6H_{12}O_6 \text{ (lævulose)}$$

Its optimum temperature is between 52 and 57°C., while even at ordinary temperature some action takes place. The ferment is destroyed at about 70°C.

Maltase changes maltose into dextrose and malto dextrin. Its optimum temperature is between 40 and 60°C and it is destroyed at about 70°C.

Zymase.—Other, deeper splitting decompositions may be visualized by considering its action on grape sugar: $C_6H_{12}O_6 = 2\ \underset{\text{Alcohol}}{C_2H_5OH} + 2\ \underset{\text{Carbon dioxide}}{CO_2}$. It is very sensitive to a temperature approaching blood heat (35°C.). Its optimum is about 10°C. The report has however been published by the Carlsberg laboratory in Copenhagen that yeast cells, which had been washed and dried in the air, then dried in vacuo at 38°C for several days, followed by 6 hr. drying at 100°C. have maintained their power to cause fermentation without significant reduction for 3 years, although all the cells were undoubtedly dead. It has thereby been proven that one of the most typical and far reaching fermentations can take place without the direct cooperation of living cells.

Diastase is the only enzyme which has been prepared in a high state of purity. It is a white powder, soluble in water, which solution has the power in a high degree to saccharify starch. According to Payers 1 part of it saccharifies 2,000 parts of starch, while according to Dubrunfaut even 100,000 to 200,000 parts will be so changed. In a dry condition it resists very high temperatures. According to Krauch it may be heated for several hours to 120 to 125°C. without loss of power; according to Hueppe it will even stand a short exposure to 159 to 162°C. Chemically, diastase appears to be an albumen of the nature of a peptone. It does not pass by filtration through porous clay-cells. Diastase splits starch into maltose and dextrin, it acts with great energy upon starch paste, which becomes limpid and transparent in 1 to 3 min. even without application of heat, and does not thereafter give a blue color with iodine; after 5 to 6 min. the red coloration of erythrodextrin also disappears and after one hour the liquid contains maltose and dextrin in the ratio of 80.4:19.6, which points to the following decomposition:

$$\underset{\text{Starch}}{C_{120}H_{200}O_{100}} + \underset{\text{Water}}{8H_2O} = \underset{\text{Maltose}}{8C_{12}H_{22}O_{11}} + \underset{\text{Malto dextrin}}{4C_6H_{10}O_5}$$

While maltodextrin is not considered fermentable, Maercker states that in the manufacture of alcohol this also will be fermented finally, because during the long primary fermentation a modifying effect of diastase becomes appreciable, by which the dextrin is hydrolyzed to maltose (or glucose).

The formation of certain acids, which always accompany, in small amounts, the products of fermentation, is probably also referable to the action of enzymes. The following formulas will make this clear:

Glucose $C_6H_{12}O_6$ = 2 $(CH_2)_2$.OH.COOH = Lactic acid
or = 2 CO_2 + 2 H_2O + C_3H_7.COOH = Butyric acid
or = $3CH_3$.COOH = Acetic acid.

Considering the lethal temperatures for all organisms discussed that cause fermentation, it will be seen that all fermentations can be arrested by heating the fermenting solution to about 75°C. It is however also possible to stop fermentation by the addition of strong acids, or alkalis, as yeast will stand only limited quantities of either. Caustic alkalis particularly are very detrimental and kill yeasts quickly.

THE MALTING-PROCESS

The purpose of malting is the production of the enzyme diastase, which has the power to convert starch into sugar and dextrin. Diastase is produced during the process of germination of grain. In general malt may be defined as a cereal, which has been subjected to the process of germination until the maximum amount of diastase has been accumulated. Germination is a biological process, during which the primary organs of the embryo (endosperm and acrospire) develop at the expense of the nutrients stored in the grain. In order to start growth it is necessary to supply water to the grain, which is done by steeping, until 47 to 48 per cent has been absorbed. This condition of saturation must be maintained during the process.

Germination may be compared to a slow process of combustion, inasmuch as carbon dioxide and water are given up with the liberation of heat. The process reminds us strongly of the process of respiration. The grain suffers thereby a loss in weight of about 3 per cent of its contents of carbohydrates.

It is necessary to provide for good ventilation, in order to prevent the accumulation of too much of the products of respiration, as by a strong increase of carbon dioxide in the malt pile the intensity of germination is considerably retarded.[1] The temperatures should be regulated so that it does not exceed 18°C. at any time or place inside of the pile of grain. The object is generally secured by taking up the malt by a shovel and letting it fall through the air in such a way that the formerly lower grains collect now on the surface and *vice versa*. If sprinkling should become necessary, not more than half a pint of water per bushel should be applied on the fourth or fifth day. The process is kept up until the acrospires show a length of growth equal to from ¾ to ⅓ of the grain. Usually in 7 to 8 days the desired results are obtained. The grains are then dried in a current of air and are finally passed through a drying-kiln where the grains are heated until the desired color is obtained on the outside, and also the well-known malt-aroma is developed. These are particularly important when the malt is destined for brewer's uses.

[1] This is analogous to the phenomena of "mass action" and equilibrium in ordinary chemical reactions.—EDITOR.

The manufacture of malt from other cereals than barley or rye is carried out on exactly the same principles and does not require a separate description. Such malts are seldom met with.

CONVERSION OF STARCH INTO FERMENTABLE SUGAR

The Mashing Process.—Under this name is understood the hydrolysis of starch by the action of diastase. In a well-made malt the amount of diastase present is not only sufficient to convert all the starch present in it, but it can convert a great deal more starch, derived from other sources at the same time. Of this property extensive use is made in technical chemistry. Brewing with malt and water alone will, however, be described first, to bring out the important points without further complications.

The brewing-kettle is charged with the requisite quantity of water and the latter warmed to a temperature of from 35 to 40°C. Ground malt, about one-fourth of the weight of the water, is now started running into the kettle and the stirring machinery is set in motion, to prevent the ground malt settling out on the perforated false bottom of the kettle. When the whole charge is in, the temperature of the mixture is brought quickly up to 42°C and held there for ½ hr. The temperature of the "mash" is now raised at the rate of 1°C. per minute, until 70°C. is reached, when the heat is checked, so as to hold the temperature stationary. It is kept so, until the "break" occurs, which is a tendency of the remnant of the malt to separate from the wort (the solution) and which is a sign to the brewer that the conversion is finished. An iodine-test for starch and erythrodextrin should be negative and thus verify the indication of the "break." The wort contains now fermentable sugar and dextrin, but no starch.

THE HOP-JACK

Brewing.—In the brewing industry the next step after the production of the "wort" (see above) is effected in large, separate copper-kettles for a two-fold purpose: to free the wort from albuminous bodies, precipitable at boiling heat, and to give it the accustomed hop-flavor and bitter taste by adding to the boiling wort the requisite quantity of hops, which are the dried, ripe, female blossoms of the cultivated hop-plant. For brewery purposes only the unfertilized blossoms can be used, as the matured fertilized blossoms have a sharp, acrid taste. The aromatic principle is mainly contained in small yellow globules, about 0.15 mm. diameter, known as hopmeal or lupulin. The female plant is propagated by cuttings. In this country it is mainly grown in the states of New York, Oregon, California and Washington, while the very choicest hops are still imported from Europe (Bohemia).

Hops are recognized as exercising a distinct preserving action on beer, aside from their main function of giving the characteristic flavor. This is attributed to the presence of "hop" resin, which has a bitter taste. There is also a tannin (hop-tannin) present, which favors the precipitation of albumen in the boiling wort. After this treatment the wort is cooled by passing it over systems of upright pipes, supplied inside with running cold water. It is then transferred to the fermenting cellar.

When we now attempt to use the same principle in the conversion of the starches of rice, grits, etc., we find, that it is necessary to cover the material with water and heat nearly to boiling, stirring well, until its starchy contents have been changed to a voluminous soft paste. In practice this is done under pressure in a separate converter, followed by cooling, after which the product is transfered to the mashing-tun. About one-fourth of the weight of the rice or grits in finely crushed malt is now added; the temperature of the mass brought to about 40 or 42°C. and the whole intimately mixed. It is often necessary at this stage to add more water, to thin the mixture to a convenient consistency for stirring. After 1 hour's standing, the temperature is gradually raised 1°C. per minute until 70°C. is reached. Owing to the smaller quantity of malt a little more time than in the case of malt alone will have to be allowed on the finishing stretch. The break will also be somewhat less distinct and it is advisable to check its progress by frequent iodine tests a few minutes apart, until the starch has disappeared. The fact is clearly demonstrated, however, that the diastase of malt has a much larger capacity for hydrolyzing starch to sugar than is required for its own starch. The liquids (worts) produced by the two mashing-processes[1] described, contain the same classes of fermentable sugars and may be indiscriminately used in the production of alcohol.

The last described mashing-process is however preferable for economic reasons, since it represents a large saving of malt, the most expensive of the raw-materials used for brewing purposes.

CONVERSION OF POLYSACCHARIDES INTO FERMENTABLE SUGARS

Acid Hydrolysis.—Of importance as a preparation for bacterial fermentation is acid hydrolysis. If dilute acids, (hydrochloric, sulphuric, and also some organic acids: oxalic, tartaric, citric) are allowed to act on starch at a temperature close to the boiling point, a complete liquefaction of the starch takes place in a short time; the solution, when cooled, gives a strong blue coloration with iodine; alcohol produces a voluminous precipitate, which, separated by filtration and washed with alcohol, will be found to be an isomeric modification of starch, amidulin or soluble starch, which can be partly obtained in a crystallized form, partly as an amorphous powder. Upon prolonged action of the dilute acid the soluble starch disappears gradually and the liquid gives a burgundy-red coloration with iodine, upon addition of alcohol a white precipitate is obtained; Fehling's solution shows reduction. At this stage the liquid contains erythrodextrin and a reducing sugar. When the heating is continued the amount of sugar increases steadily, until finally no iodine-reaction can be obtained, the erythrodextrin has passed over into achroödextrin, which also gradually disappears and there finally remains besides more or less sugar, according to the duration of the heating, a body "Gallisin" ($C_{12}H_{24}O_{10}$) (Schmitt and Cobling). The end product of the action of the acid is always dextrose. The process may be represented by the formula:

$$\underset{\text{Starch}}{C_{120}H_{200}O_{100}} + 20H_2O = \underset{\text{Dextrose}}{20C_6H_{12}O_6}$$

The application of this process under pressure has become of commercial importance in the manufacture of alcohol from wood shavings, the high temperature obtained permitting the hydrolysis of compounds closely related to cellulose, with formation of fermentable sugar.

[1] With malt alone, and a mixture of starch and malt.

ALCOHOLIC FERMENTATION

By fermentation is understood a sequence of highly characteristic processes, which, with the aid of an active reagent present in relatively small quantity, cause the decomposition or alteration of large quantities of organic substances. The active reagent is called "ferment" but we know now that very different kinds of ferments may enter into a reaction. They may be microorganisms or bodies related to albumen. Therefore a distinction is made as between organized ferments and enzymes. By fermentation in a narrower sense is now understood such decomposition as may be caused by the activity of living microörganisms. The process of fermentation involves three classes of bodies.

1. The substratum or substance to be acted upon,
2. The microorganisms, as the cause of the reaction by their life processes;
3. The products of fermentation.

The activation may be caused: (1) by budding yeast or blastomycetes; (2) molds, or fungi, hyphomycetes; or (3) by bacteria or schizomycetes

While all three classes of microorganisms may cause alcoholic fermentation, only the class of blastomycetes is of controlling importance for the industrial production of alcohol, while in acid-fermentations and in water purifications bacteria play the most important part. We shall first consider alcoholic fermentation The substrata for alcoholic fermentation are various kinds of sugar, which by passage through the bodies of blastomycetes, participating in their life-cycle, are decomposed into alcohol and carbon dioxide and minute quantities of succinic acid and glycerin. The main part of the process may therefore be presented by the following equations.

$$C_{12}H_{22}O_{11}(\text{cane sugar}) + H_2O = 4C_2H_5OH + 4CO_2$$
$$C_6H_{12}O_6(\text{glucose}) = 2C_2H_5OH + 2CO_2$$

From 100 parts of cane sugar therefore 53.8 parts of alcohol and 51.46 parts of carbon dioxide would be produced, if no other reactions took place, while from 100 parts of glucose the corresponding figures are 51 parts alcohol and nearly 49 parts carbon dioxide. These figures are, however, never reached. Jodtbaur gives the following figures for actual results obtained.

Cane sugar	51.11 per cent Alcohol, 49.03 per cent CO_2
Maltose (anhydrous)	51.08 per cent Alcohol, 49.04 per cent CO_2
Dextrose	48.67 per cent Alcohol; 46.54 per cent CO_2

The figures for cane sugar agree with those found by Pasteur. The microörganisms predominantly employed in alcoholic fermentation are known as "cultured yeast," which consists of immense numbers of cells of *saccharomyces cerevisiæ I* (Hansen). Under the microscope this organism is shown to be a slightly elliptical cell, growing in groups. In order to avoid untoward reactions and obtain constant results, the use of this yeast, raised under proper conditions from one single cell, has been successfully introduced in the technical field, particularly in the brewing industry. By rigidly excluding acid-producing bacteria, the formation of more than traces of acetic, propionic, lactic and succinic acids is successfully avoided.

In the distilling industry the same care in regard to yeast need not be exercised, since the fermentation is followed by distillation, which is so regulated that most of the impurities, including higher alcohols, produced by microbes, are eliminated. Moreover, in this latter case the formation of certain esters is desirable, as they play an important part in the development of the final aroma. A slight acidity of the freshly

distilled spirits is therefore necessary, to induce formation of esters, by combination with alcohol during the storage of the distilled spirits in wood. Ethyl acetate is the principal ester formed.

YEAST

All microörganisms are distinguished from other organisms as being of a simple structure, which consists in one cell for the individual. In spite of the apparent simplicity they possess as a class an astonishing amount of energy which manifests itself in the causation of fermentation, in putrefaction and in the production of infectious diseases, as the case may be. They are essentially plantlike and may be divided, as has already been said, into three main classes:

1. Mold fungi or Hyphomycetes.
2. Yeast fungi or Blastomycetes.
3. Bacteria or Schizomycetes.

We shall here consider the second class, as used in the fermentation of worts, the products of the mashing-process, which has been previously described. It is the general aim in the industries here comprised, to have a reliable, powerful yeast, which will do the work of producing alcohol from the sugars presented to it, in the minimum of time and without leaving any sugar behind, *i.e.*, do it economically. This problem has been of such vital importance to the industries of brewing and distilling, that even long centuries ago conditions had been worked out empirically, how to protect these industries against untoward (infectious or other) influences, which might impair the efficiency of their most important laborer. It has been left however to the ingenious studies and labors of scientists of the second half of the last century, among whom I may name Pasteur, Liebig and Buchner, to reduce the problem successfully to a solid basis which has placed the technic of the industry in a position to regulate the processes at will and at all times.

In the first instance a certain mechanical purity must be aimed at. A first class yeast must only contain cells of *saccharomyces cerevisiæ I* to the exclusion of all of the numerous varieties of this species and further it should not contain any other kinds of microorganisms, particularly no bacteria. The only way to reach this point is to raise the stock of yeast from one single cell of the required species, under exclusion of any and every chance infection.[1] This is accomplished by dividing a small quantity, say 1 drop, of yeast in a large quantity of sterile water, say 1 quart, under aseptic conditions. After closing the flask with a tight-fitting, sterilized glass stopper, the mixture is shaken until homogeneous. Then small quantities of this water, 0.1 c.c. each, are transferred by a sterilized platinum-loop to sterilized, cotton-plugged test-tubes, containing wort-gelatin, which has been previously liquified by placing the tubes in water of 30°C. just for a sufficient time to melt the gelatin. The technique of this is as follows. The gelatin-tube is held between thumb and index finger of the left hand in as nearly a horizontal position as the contents will permit; the cotton plug removed and placed between the third and fourth fingers of the left hand. A platinum loop (fused into a piece of glass tubing) is then grasped with the right hand, heated in a gas or alcohol flame, and cooled. A helper now lifts for a moment the stopper of the flask, containing the diluted yeast, the platinum loop is inserted with the right

[1] The processes of producing a pure culture are described in detail, since it is obvious that the method is of general application and that it is the basis of all fermentation industries —EDITOR

hand, the drop removed and transferred at once into the open gelatin-tube. The helper immediately closes the yeast flask, while the operator replaces the cotton-plug with the right hand in the gelatin-tube. These manipulations are repeated for every gelatin-tube that it is desired to seed. The tubes are now shaken and each emptied into separate, sterilized, cool, Petri dishes. The covers are replaced at once, the gelatin distributed evenly by gentle tilting and the dishes removed to an icebox, where the gelatin quickly solidifies.

The various cultures in the Petri dishes should be examined daily looking through the cover, without raising it. After several, usually 3 to 4 days, one may see in some or all of them little white dots. Each represents a culture from one cell. While waiting for them to grow to distinct visibility, one must prepare a number of sterile

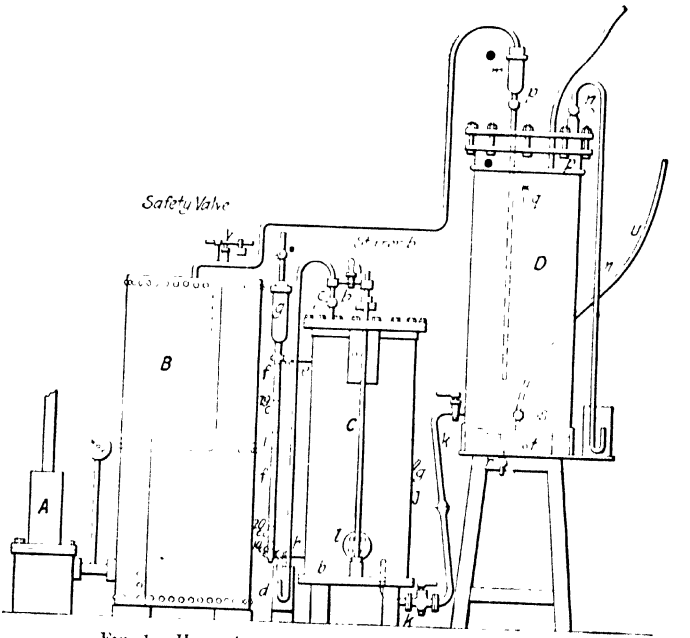


FIG 1 — Hansen's apparatus for pure culture production

flasks, say six or a dozen, containing clear, sterile, sweet wort; or if such is not at hand, a clean sterile sugar solution of about 10° Bal. density, containing some nutrient salts. For this purpose dissolve in every 100 c.c. of sugar solution 1 g. ammonium nitrate; 0.5 g. potassium-hydrogen phosphate, HK_2PO_4; 0.05 g. precipitated calcium phosphate (Ca_4HPO_4); and 0.5 g. magnesium sulphate, cryst. From the flasks are selected a sufficient number to make cultures from the Petri dishes. A piece of platinum wire, rather stiff and about 1 in long, is fused into a piece of glass tubing as a handle. A Petri dish with a round dot or dots is placed near one of the flasks, containing nutrient solution. A lighted Bunsen-burner should be at hand. The platinum wire is sterilized and cooled, the cover of the Petri dish lifted, the small culture selected quickly which looks healthiest; touched with the point of the platinum wire, so that a

little bit of the colony will adhere to it, the wire withdrawn from the Petri dish and the lid replaced quickly. The cotton plug is then removed from the sterile flask, the tip of the platinum wire lowered into the liquid, stirred about for a few seconds, withdrawn, and the cotton plug replaced quickly. With one assistant one can easily make a dozen inoculations in a couple of minutes. The flasks should be kept in a room at about 60 to 70°F.; in hot weather placed in an icebox. If observed daily, one or another will show signs of fermentation beginning after a day or two, which will increase and come to an end in about a week. These are the first pure yeasts to start a supply from. In order to raise it from small beginnings one must have a yeast-propagating apparatus of sufficient capacity for one's requirements. Before starting the yeast in it, it is necessary to make a careful microscopical examination to make sure that it is really a pure culture. If this should not be the case, another of the little fermenting flasks, should be tested and if necessary another, until one is found which is surely a pure culture of *saccharomyces cerevisiæ I.* If one fail in this, one must discard the whole work so far done and start all over again, until one surely has a pure culture. The propagation of the pure culture on a commercial scale must then take place in one of the standard forms of propagation apparatus, of which Hansen's is the prototype. This will be described in detail in order to show the essentials in its construction.

He describes it in "Practical Studies in Fermentation" as follows: "As shown in the accompanying illustration the apparatus consists of two main parts and the connecting tubes, namely: The fermenting cylinder *C* and the wort-cylinder *D*. The details of the airpump and airholder are not shown in the drawing. The airpump *A* is driven by machinery and draws air through a filter in order to effect a preliminary purification. The airholder *B* is provided with a pressure gauge and a safety valve. It is charged with air under a pressure of from 1 to 4 atmospheres. The pipes must be fitted with cocks at suitable points for removing water, which will collect in them. This is of especial importance in the case of the pipe between the airholder *B* and the filters, *g* and *m*. These are best united by metal tubes with the air pipes. If metal tubes are used they should naturally possess some degree of elasticity and must be so arranged that the filters can be readily fitted and disconnected.

"Through the top of the fermenting-cylinder *C* passes a stirrer *b*, the lower end of which is fitted with two blades, one carrying a sheet of rubber in such a way that when rotated it comes into contact with both the bottom and the sides of the cylinder. From the top there passes a doubly bent tube *c*, and by opening its cock, connection is made with the inside of the cylinder. The lower free end of the tube dips under water in the vessel *d*.

"A little below the top is a horizontal tube *e* provided with a cock, by means of which the inside of the cylinder is connected with the vertical glass tube *f*. This is connected at its upper end with the filter *g* and at its lower end with a second cock and similar horizontal tube *h* to that described above. The top mark on the glass tube is 79 cm. from the bottom of the cylinder, the next 20 cm., and the lowest 10 cm. When filled to the top mark, the cylinder holds about 1½ barrels or 46.5 gal. or 176 l. The glass tube is fixed into the cocks *e* and *h* by a packing of hemp or cotton wool with vaseline; rubber is not suitable, as it is hardened by steam. The filter *g* consists of a metallic capsule containing a tightly packed plug of cotton wool 22 cm. long and 3 cm. in diameter. The plug contains at least 35 g. of cotton wool; the addition of a little more is immaterial. If firmly pressed in, the capsule will hold 50 g., but that much is unnecessary. The filter is closed above by means of a cover, which is screwed on and which is connected with the tube from the airholder. Before the fitter is screwed on, it is sterilized by heating it for 2 hrs. at a temperature of about 150°C.

At the opposite side of the cylinder there is a small tube *j* scarcely 1.5 cm. long fitted with rubber tubing, the latter being closed by a pinch cock and a glass stopper. Passing from the bottom of the cylinder is a tube *k*, through which connection can be

made with the wort cylinder *D;* this tube is made in two pieces to prevent too great rigidity and in addition to the two large cocks shown it is provided with two smaller ones, which are made use of during the process of steaming described below, partly for running off the condensed water and partly for introducing steam.

The cock shown at *l* is for withdrawing the beer and the yeast. The valve is screwed down in opening the cock and is screwed up when this is closed. In the figure it is closed. Its construction prevents infection from occurring while the liquid is being drawn off as the liquid cleanses the cock on passing through it. The pipe carrying the cock is passed through the side of the cylinder and is bent toward the bottom, its end being 3.5 cm. above the latter. It is, in short, so arranged that no air from without can enter the cylinder, while its contents are being drawn off.

"The wort cylinder *D* must be raised somewhat above the level of the fermenting cylinder. (The wort can, of course, also be forced into the fermenting cylinder by means of compressed air, but in this case the wort cylinder must be provided with a safety valve.) Its height is also greater than that of the latter, but its diameter is the same. At the top is a filter *m* exactly as at *q*, and connected with it is a pipe (indicated by dotted lines) passing inside the cylinder. The lower closed end of this pipe has some small perforations through which the air finds an exit after passing through the filter. The tube *n* corresponds with the tube *c* of the first cylinder, and like the latter its open end dips into a vessel of water *o*. In the case of the wort cylinder it is very important that the bore of the tube *n*, and of its cock should not be too small, in order that they may not become choked by hops and other matter; a suitable diameter for the tube is 1.5 cm. Around the upper portion of the cylinder, a little below the top, there is a pipe in the form of a ring *p*, the inner side of which is provided with small perforations. One end of this pipe is closed and the other is connected with a cold-water tap. In addition to the cocks on the connecting pipe *k* between the two cylinders, the wort cylinder has three others *q*, *r*, *s*. The cock *s* is for the introduction of the wort and is put in connection with the wort main *U* between the copper and the cooler. The cylinder stands in a shallow tray provided with an outlet *t* for the water, which flows over the sides of the cylinder while the latter is being cooled. The dotted lines at *t* show the bars on which the cylinder rests, and also the ring-like portion and bottom of the cylinder.

"If the fermentation cylinder is not standing in a room with even temperature it is necessary to arrange it in such a manner that the temperature of the liquid contained in it can always be controlled, and that it can be lowered at will.

"This is done by means of the jacket, shown around *C'* covering not only the sides, but also the bottom of the cylinder; the bottom of the jacket is provided with screws and can be removed, when it requires cleaning. For the introduction of a thermometer there is a tubular aperture through the jacket and the side of the cylinder. The jacket is provided with a tap near the bottom, forming the inlet for cold water, and another near the top and on the opposite side for its exit; a third tap at the bottom serves for removing the sediment which is gradually deposited by the water. The wort cylinder is here also provided with a jacket, which however can very well be omitted, as the perforated ring serves the same purpose sufficiently well. Nevertheless the jacket has the advantage that it encloses the water from the ring so that the operator is not liable to receive splashings. It adds, however, considerably to the cost of the cylinder and makes it more cumbersome to manipulate. The middle portion of the cover is made of copper and is provided with a brass flange with 12 bolt holes. Between the cover and the collar of the cylinder a rubber washer is inserted and fits into a groove, a perfectly air-tight joint is thus insured.

"In order to prevent the stirrer from being raised out of its bed at the bottom of the cylinder while in use a ball socket is provided. The axis ends in a ball which rests in a hemispherical socket and two pieces, accurately fitting the upper portion of the

ball are bolted on; the axis can be rotated but cannot be raised from its socket. With regard to the tinning of the cylinder, it must be pointed out that the tin should not contain an appreciable amount of lead. If this should be the case, the yeast grown in the apparatus will, according to Prior, be unsatisfactory.

"In putting up the apparatus it should be borne in mind that it should remain undisturbed in its position. When possible, it will be best to place it in the fermenting cellar. There is then, as a rule, no trouble with the regulation of temperature and in drawing off the beer and the yeast there will also be less labor involved, for those employed in the intervals do other work close at hand. If the temperature in the cellar is below 6°C. it is advisable to have the fermenting cylinder jacketed.

In putting up the apparatus it is, of course, necessary at once to consider whether one or two fermenting cylinders are to be employed; in any case a single wood cylinder will suffice. The apparatus having been erected, it is necessary first to test the cylinder in tightness. Steam is cautiously introduced through *K*, while all other cocks are closed: also water under pressure may be employed.

Sterilizing the Apparatus.—Before the apparatus is set working, the two cylinders must be thoroughly sterilized, also the connection between them and the pipe through which the wort is to pass to the wort cylinder. This is accomplished by passing a strong current of steam through the system. The filters are sterilized, as previously described, in a sterilizing oven. The fermenting cylinder is sterilized by steam through one of the cocks on pipe *K*. While high pressure steam is passing the different cocks are alternately opened from time to time, so that the steam can escape through them as well as through the bent tube *c;* this operation requires half an hour. Shortly before this the filter is screwed on and then all cocks are closed except the one in the bent tube *c*. Simultaneously the cock of the filter is opened to allow air through it, *g*, and tube *h* into the cylinder. The latter cools as the air enters and the steam is gradually turned off. The cooling is thus effected by the current of air, which mixed with steam escapes through bent tube *c*. As long as steam is seen to escape, the vessel *d* with water is not required; this functions only at a later period as an indicator. If the steam were shut off suddenly, there would be danger of the filter not admitting sufficient air to prevent a reduction of pressure due to cooling and the result would be the inspiration of impure air into the cylinder or the collapse of the latter by the external pressure of the atmosphere. Under the conditions mentioned and at the usual temperature of a fermenting cellar, the cooling takes about 2 hrs. With regard to the small water vessels *d* and *o* surrounding the bent tubes, their only function is to indicate the direction of the air current, be it outward or inward.

Operation of the Apparatus.—The wort cylinder and its pipes *s*, *q* and *k* are sterilized in the same manner, but the process of cooling is here omitted. When the steaming is nearly finished, the cock of the air filter is opened and wort is admitted. The latter is the ordinary hopped lager-beer wort, which has been sterilized by boiling in the copper, and is run as hot as possible through pipe *u* and cock *s* into the cylinder. Shortly before the steaming is finished the pumping of the boiling wort on to the cooler is commenced and 10 min. later cock *s* is opened. The wort is allowed to flow into the cylinder until it reaches the upper cock *q*, when cock *s* is closed. It is advisable to place a small bucket under cock *q* to catch any wort which may run out. When this occurs the cylinder contains the desired volume of wort. The hot steam and air escape

partly through *q*, partly through bent tube *n*. It is advisable to run off the first small quantity of wort, which enters the cylinder, through cock *r*, as it is mixed with condensed water, which gives it a disagreeable taste. When the cylinder is finally filled with wort as desired, cocks *q* and *s* are closed. Air sterilized by passing through the filter is now forced through the hot wort before cooling is commenced, and this aeration is continued during cooling. Generally a pressure of from 1 to 2 atmospheres in the air tank suffices. It is merely necessary that the sterile air in the cylinder should always exert a slight pressure over that of the atmosphere, thus preventing the drawing in of any impure air, and to insure the taking up by the wort of the fullest amount of oxygen possible. It is evident that the operator must not forget to first open the cock *n*. If this is not done, there is a risk of damage to the apparatus.

"As soon as the wort is ready for cooling, the perforated ring *p* is connected with a water tap and the sprinkler allowed to play against the outside of the cylinder until the temperature of the wort is reduced to about 10°C. In an ordinary fermenting cellar this takes about 1 hr.; further cooling must be effected by ice water. The air is passed through the wort continuously, and in escaping through the bent tube carries some wort along; the rousing of the wort produces much foam, but this never gives rise to contamination. The aeration must, however, not be too vigorous or there may be too heavy a loss of wort. It is only when the wort has cooled to 11 to 12°C., that foam passes through the tube, which may be moderated by pouring warm water in vessel *o*. The wort, now ready for fermentation is transferred through pipe *k* to the fermenting cylinder.

If it is desired to free the wort from most of its suspended matter it may be allowed to settle for an hour, before drawing it over. To guard against the entry of impure air the filter must be left slightly open during this time, at the end of which a considerable amount of solid matter will have settled out, of which only a small portion will be carried over, as the mouth of pipe *k* is at a sufficient height from the bottom of the wort-cylinder.

The wort introduced should not reach above the small tube *j*, through which the yeast is introduced. The yeast is previously collected in large two-necked glass flasks or tin cans and in the transferring operation a bunsen burner or a spirit lamp may be made use of.

"The stirring apparatus is now set in motion and the yeast mixed well with the wort. As soon as this is done any remainder of the wort is added until its level rises to the upper mark on glass-tube *f*, the volume then measuring about 1½ bbl. The column of liquid in this tube is forced by pressure of air, passing through the filter into the cylinder, the cock on the upper horizontal tube *e* being closed and the cock on the lower tube *h* opened. When it is not desired to continue aeration during fermentation the latter cock is closed, but only after the cock above the filter has been closed.

"After about 10 days the desired portion of the newly formed yeast can be drawn off. It is here assumed that the cylinder has been exposed to the ordinary temperature of the fermenting cellar; if the temperature has been higher, the yeast will be ready for removal in a shorter time.

"The beer is run off at cock *l* and when froth appears this is closed. Some wort from the wort-cylinder—which by this time has been recharged with wort for a new fermentation—is now passed in until the level rises to the second mark from the bottom on glass tube *f*. The yeast is now well stirred up by means of the stirring apparatus, and the mixture of yeast and wort is drawn off into a perfectly clean vessel (cleansed with hot water and then steamed). When the level of the liquid has sunk to the lowest mark on the glass tube, the cock is closed and wort again run in to

the second mark. The yeast is again stirred up and drawn off to the lowest mark; the amount withdrawn now measures about 13 gal. The portion remaining behind is sufficient to start a new growth.

It is advisable to have two marks in the vessel, into which the yeast is drawn off, one indicating 6½ gal. and the other 13 gal. Great accuracy is not required. The yeast obtained is sufficient to pitch 8 bbl. of wort and a new fermentation is started as soon as possible in an ordinary, well cleaned, fermenting vessel. If this can not be done at once, the vessel containing the yeast must be covered over and set aside in a cool and clean place."

ALCOHOLIC FERMENTATION

Practical Applications.—We have now discussed all the preliminary processes and their products up to the process proper of fermentation and shall now describe the latter on a broad basis, *i.e.*, under such conditions as are essential for the production of alcohol, no matter what its final use may be.

In the fermenting cellar usually a temperature of from 1 to 2°C. is maintained, in warm weather by artificial refrigeration. We start with 10 to 12 lb. of pure culture yeast and 8 bbl. of a wort of a gravity of 14°Balling (sp. gr. 1.0572) of which about 10°Bal. represent its contents of fermentable sugar.

The wort is contained in a cylindrical wooden tub, about two to three times as high as its diameter and filled to about 6 in. from its top, which is open. We now "pitch" the yeast, *i.e.*, we introduce it, after diluting it with its own volume of wort, at the top and cause its thorough distribution throughout the wort in the tub, best by agitating with a lively current of filtered air. After 18 to 24 hr. some bubbles of gas may be observed to rise to the surface. During this stage of the process a good deal of heat is generated in the fermenting tub, causing a gradual rise of temperature to about 8°C. On top of the wort a head of material consisting largely of albuminoid matter gathers and should be skimmed off. When removed, the surface of the wort shows a fine white froth. The fermentation now increases rapidly in strength and becomes rather violent during the third and fourth day, when large masses of foam collect on the top. From about that time the activity diminishes and comes apparently to an end after 8 to 14 days, when the foam collapses and the liquid beneath becomes visible first in patches, then generally. It is now cooled to 4°C.

This is the end of the main fermentation. When now, after the yeast has settled, the fermented product is removed to a storage vat or chip-cask, it will be found, that at 1 to 2°C. a gentle after fermentation (of malt-dextrins) takes place, sustained by the floating yeasts.[1] This is however only important in beer brewing, as it has a beneficial influence upon the aroma and taste of the beer. When this after-fermentation is over an examination of the product will show a specific gravity of about 1.01, the matter in solution will be about 2.60 per cent and alcohol from 5.5. to 6 per cent. The product of the fermentation will measure about 230 gal., which will yield upon distillation about 25 to 27 gal. of "proof" spirit or its equivalent of any desired strength.

DISPOSITION OF YEAST, AFTER FERMENTATION IS FINISHED

The disposition of used yeasts in the breweries is a sore spot in their economy. Of course as long as yeast maintains a condition of relative purity, ascertained by microscopical control, it may be used again until a point is reached where it

[1] Of which sufficient always remain suspended to start the process again.

better be discarded, or until it is pushed out of line by the pressure of newer cultures, for the multiplication of yeasts during fermentation progresses at an enormous rate. It is finally disposed of by washing it down the sewer. If it were not for the bitter hop taste, which clings to it tenaciously, it might find use as an important adjunct to cattle foods, or it might conceivably even be used as a concentrated human food. So far no practical way is in sight to make such uses possible.

The case is different with yeast from distilleries, which is entirely free from this objection and is consequently eagerly bought by manufacturers of yeast-cakes for baking-purposes.

FERMENTATION OF GRAPE-MUST

In the art of making wines from fruit juices the processes usually applied are more primitive. The unit for a fermentation is the barrel which may be of great diversity of size. The barrels are set up in the well known type of wine-fermenting cellars, which also vary greatly in size and capacity. They must have a fairly cool uniform temperature, but are not artificially cooled. No yeasts are raised in cultures, but the germs are either allowed to enter with the must coming from the fruit-press, having been derived from the skins of the fruit, where they always are found, or the introduction may take place from the atmosphere of the cellar, where frequent fermentations have previously taken place and where yeasts and other microbes are always present. The process of fermentation is under such conditions as to be dependent largely upon accident, time, character and strength of infection, and its cycle usually represents the time of several months, instead of about 2 weeks, as stated in the preceding sections. The hazard of introduction of undesirable yeasts or dangerous bacteria may prove a great danger to the product.

The fermentation is slow in starting and will only gradually assume livelier proportions, in so far as the development of a sufficient quantity of yeast in the casks progresses more or less slowly. The predominating desirable yeast is *saccharomyces*

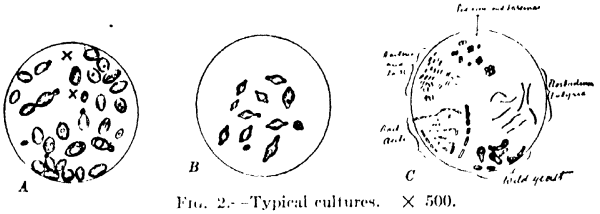


FIG. 2.—Typical cultures. × 500.

A. Saccharomyces cerevisiæ I (The two cells marked X are dead.) *B*. Saccharmyces apiculatus. *C*. Pediococci and sarcinæ, lactic- and acetic-acid bacteria, clostridum butyrici and wild yeast.

apiculatus. Its cells are smaller on the average than *saccharomyces cerevisiæ*, ellipsoidal (lemon shaped) in form, with the ends extending and frequently rounded off, bulb-like. It ferments only dextrose. Since it does not form spores, it is really not a true saccharomyces. It occurs commonly on ripe fruits and almost always in wine-yeasts. Admixtures of *saccharomyces ellipsoideus* Hansen or allied species are

frequently present. Besides these yeasts generally a multitude of other micro-organisms are found, since anything which will settle on fruits or berries has a good chance to get into the cellar with the must.

According to geographical location these mixtures of microorganisms will vary and so will the product. This is perhaps the reason why wine fermented in certain cellars is likely to show fairly constant characteristics of "bouquet" and "aroma" for many years.

These observations may even be extended to all wine-producing countries, like France, Italy, Greece and many others, whose products differ materially from the standpoint of the "connoisseur," although their grapes do not vary much. Still more strength is given to these deductions by the fact that, when foreign grapes are imported into a country, to be there used to increase the wine production, they do not produce the kind of wine usually produced in their home, but they become "naturalized" and produce wines identical with or at least very similar to the wines of the country where they are fermented. It is often quite impossible to distinguish the two products. There is therefore a hint at the possibility of producing wines with characteristic bouquets at will by using yeast-mixtures of known varieties, containing also known species of bacteria.

Experiments on record, made on an industrial scale, a number of years ago, have proven that it is even possible to produce by a suitable selection of yeast-mixtures, from a wort made from grains, wine-like products, showing characteristics of a grape-wine, produced with the same yeast from grape-must. Products offered in various markets under the name of malt-wines belong to this class.

The conclusion may therefore be drawn in a general way, that, while the alcoholic strength of a wine will correspond closely to the fermentable sugar furnished by the grapes, its aroma (bouquet) depends upon a secondary action and is referable to the building up of certain esters and related bodies, by a synthesising action of micro-organisms, not necessarily yeasts, but probably predominantly of certain acid-forming bacteria, which in the presence of alcohol, can also form esters. This last process of forming the bouquet is much slower than the process of fermentation and requires several years at the relatively low temperature of wine cellars.

In order to control the ripening process the action of the acid-forming bacteria must not be allowed to proceed without a check. As it is impossible to arrest their activity by heat, the purpose is usually attained by introducing at the proper time a moderate quantity of a solution of isinglass in a restricted quantity of water, so that it forms a stiff jelly. It is allowed to spread over the level of the wine and to sink slowly to the lowest portion of the horizontal cask, carrying along all matter in suspension.

The process, above described, may serve as a model for other fruit juices, like apple-cider or pear-cider, to be converted into their respective "wines."

Lactic Acid Fermentation.—The spontaneous curdling of milk, which takes place regularly upon the latter standing exposed to air, is a separation of casein by lactic acid. Lactic acid, which is not contained in fresh milk, forms by decomposition of lactose (sugar of milk) under the influence of organized ferments, the most active of which has been named lactic acid bacteria. A number of different bacteria may cause lactic acid fermentation. The organism shown in the accompanying illustration however has this faculty in such preponderating degree that it is known under the name of *Bacillus acidi lactici.*

As in the case of any fermentation the "optimum" conditions for the multiplication of the fermenting organism must be supplied. A pure solution of milk sugar exposed to the air does not ferment.

The lactic acid ferment requires for its nutrition, like yeast, albumen and certain

salts, mainly phosphates and chlorides of sodium, potassium and calcium, which are offered in milk in abundant quantities.

As in the case of alcoholic fermentation, which takes place only slowly at low temperatures, the lactic acid bacteria develop slowly at low temperatures, so that by sufficient cooling the acid-formation can be much retarded. Like alcohol yeast the lactic ferment is destroyed at a higher temperature. At 45.4°C. lactic-acid fermentation is arrested.

Lactic-acid bacteria are also very sensitive to their own product, so much so, that the formation of lactic acid will stop when a liquid contains 1.6 per cent of lactic acid (Richet). Kueppe describes the *bacillus acidi lactici* as oval bodies, which under



FIG. 3.—Lactic-acid bacteria. ×400.

strong magnification resolve themselves into short, stout rods, 1 to 1.7μ long and 0.3 to 0.4μ thick. They are mostly found in pairs. Before partition they may become as long as 2.8μ. They form spores. Micrococci forms are never seen.

At temperatures below 10°C. the bacillus does not develop. The optimum is between 35 and 42°C., at 44.5 to 44.8°C. retardation sets in and at 45.4°C. its activity is arrested (death point).

Besides lactic acid and a little carbon dioxide no other products are formed. According to Kueppe only 0.8 per cent lactic acid as a maximum is formed. Lintner gives as the most favorable temperature for the development of the ferment and the production of acid, 40 to 50°C. He gives a concentration of about 1 per cent of lactic acid as the limit of growth and fermentation.

If continuous production of lactic acid is desired it is therefore necessary to keep the medium neutral by the presence of an excess of calcium carbonate, so that all lactic acid will be converted into the calcium salt, as fast as made.

Lactic acid bacilli are almost always present in the air and can be readily attracted by any suitable medium, as wort or glucose solutions. The decomposition of glucose by lactic acid bacilli may be represented by the following equation:

$$\underset{\text{Glucose}}{C_6H_{12}O_6} + 2O_2 = \underset{\text{Lactic acid}}{2C_2H_6O_2.} + 2CO_2$$

Byproducts except a little carbon dioxide do not appear in this process.

The process in its technical execution is simple, when once properly started. To begin with a "pony" must be allowed to absorb lactic acid bacilli from the air, or better, must be infected from a pure culture. After being kept for several days at a temperature of 40 to 45°C., best 42°C., the sugar solution will be found in a lively

state of fermentation. It may be kept thus, until the acidity indicates about 1 per cent, or a little over, of lactic acid.

Meanwhile a fermenting-tub is charged at the bottom with powdered calcium carbonate, enough to neutralize the maximum of lactic acid expected, and is then filled with wort or sugar solution (glucose) to about 6 in. from the top. The fermentation room should have a temperature of not less than 40°C. and not over 45°C., best 42°C., and must be kept within these limits. The pony is then transferred into the fermenting-tub and well distributed by stirring.

The fermentation is allowed to proceed until it ends by exhaustion of the nutrient solution, which will be the case in from 7 to 10 days. The lactate of calcium is then separated from the waste liquor, of which a sufficient portion is set aside as the next "pony," while the balance is discarded.

The lactate of calcium is washed free from adhering mother liquor with a small quantity of clean water and is then decomposed by a calculated quantity of dilute sulphuric acid of about 25°Bé. strength. To every hundred pounds of the lactate 176.6 lb. of 25°Bé. sulphuric acid will be required. The solution of lactic acid is separated from the gypsum in a filter press and is further concentrated by evaporation to any required strength. It has been usually the practice to concentrate the acid to a specific gravity 1.24, but commercial lactic acid is often found in the market with a specific gravity of 1.21 which corresponds to 75 per cent of lactic acid.

ACETIC ACID FERMENTATION

Vinegar from Alcohol.—It is not intended to discuss the possibilities of synthesizing acetic acid from all the substances wherefrom chemistry has succeeded in producing it, but the practical standpoint will be adopted of explaining briefly the chemical changes which the most important materials have to undergo in order to furnish the acid and then to describe the production of acetic acid in the usual, dilute form of vinegar by a peculiar process of fermentation, caused by certain bacteria, mainly by *bacillus aceticus*. The age of the process does not detract from its intrinsic interest, as even today some points exist in it which would stand further elucidation. The starting point is the same class of material, which has been before discussed in the manufacture of alcohol, to wit, saccharine solutions whose sugar has been split by fermentation into alcohol and carbon dioxide. The starting point in a narrower sense is alcohol and its continued further fermentation may be visualized by the formula:

$$\underset{\text{Alcohol}}{C_2H_5OH} + \underset{\text{Oxygen}}{2O} = \underset{\text{Acetic acid}}{CH_3.COOH} + \underset{\text{Water}}{H_2O}$$

In the destructive distillation of wood and similar organic material much acetic acid is formed, which before purification is then known as pyroligneous acid. After purification, usually by production of the calcium salt, which forms an important article in trade, the purest kind of acetic acid is produced, which solidifies below 16.7°C. to a beautiful mass of crystals, whence it is known as glacial acetic acid. Most of the rather dilute solutions of acetic acid known as vinegar are made from grains or fruit juices, apple juice being a favorite among the latter. The grains are first subjected to a mashing process and an alcoholic fermentation, while fruit juices are directly subjected to the oxidizing process. The strength of the alcohol should not be over 10 per cent, but is often much weaker. In practice from 4 to 7 per cent is often found suitable.

nversion to be a process of slow and incomplete oxidation caused by the life-process of *mycoderma aceti* or lately more frequently called *Bacillus aceticus*. Mycoderma species are to be found everywhere in the air. If they come in contact with substances which support their lives, they commence to multiply rapidly. The best conditions for their growth are furnished by an aqueous liquid containing about 4 to 5 per cent alcohol, 1 per cent acetic acid and some nutrient salts (ammonium phosphate, potassium, phosphate and magnesium phosphate, about 0.1 per cent of each). Sometimes good results are obtained by adding infusions of bread, malt, or raisins, instead of the salts.

The temperature of the fermenting room is kept at between 27 and 32°C. as an optimum. During the process a great deal of heat is generated and it is advisable not to allow the temperature of the solution to go beyond 35°C. as this will cause loss of alcohol. At 45°C. the process stops by the killing of the active organism. Therefore means must be provided to keep the temperature within above limits, in winter by heating; in summer by lively ventilation. Losses caused by neglect in this direction may be as high as 20 per cent. The duration of a vinegar-fermentation depends largely upon the temperature. Between 22 and 30°C. it is given as 8 to 16 weeks, at 30 to 35°C. as 4 to 8 weeks and at 35 to 38°C. as 2 to 4 weeks.

The following description is given in order to show a simple apparatus as an effective vinegar-former. It consists of a large tub, made of oakwood, about 10 ft. high, measuring 4 ft. at the top and 3½ ft. at the bottom. Eighteen inches from the bottom is a perforated false bottom, resting on a strong rim of beechwood. Two inches below this are bored 8 to 10 holes, distributed evenly around the circumference. In order to prevent leakage the holes incline slightly towards the inside of the tub. Twelve inches below the cover is the second strong rim of beechwood, which carries another false bottom set in watertight and provided with several hundred narrow perforations. These perforations are about 1 in. apart. This sieve-bottom is for the purpose of dividing evenly the alcohol-vinegar-mixture over the chips below. Often these perforations are further restricted by placing pieces of twine, 2 to 3 in. long with a knot tied at the upper end as a support, so as to allow only single drops of the liquid to fall on the chips. The solution is poured on this bottom, is gradually taken up by the twine, and drops down in a regular distribution. The space between the two bottoms is filled with wood-shavings. In the upper portion of the latter is placed a long right-angle thermometer, whose bulb reaches to the axis of the tub, and whose scale is on the outside. The upper perforated cover carries six 1-in. holes, in which 6-in. glass-tubes are inserted, which serve as ventilators to remove exhausted air from the chamber below. Holes below the lower false bottom admit fresh air. An oak cover closes the top. It has a funnel-shaped opening in the center, which may be more or less closed at will. Liquid is poured in through it and the draft is there regulated to suit conditions.

After the converter is ready, hot vinegar is passed through it for several days to soak the chips and the inside of the tub. The alcohol-vinegar-water-mixture is now poured through the funnel-opening of the cover at a rate of 1½ to 2 gal. per hour. It divides itself over the chips and flows gradually and slowly to the bottom. The procedure is repeated in either the same tub or alternately through another one, constructed in the same way, until the desired degree of acidity has been obtained. In the beginning the working-room is heated to 38°C. and the charge to 50 to 52°C. When working regularly, the room is kept at 21°C. and the liquid at 26 to 27°C.

By the rapid oxidation inside of the tub the temperature rises to 38 to 42°C. The thermometer furnishes the best control of the process. After two passages through the tubs, the liquid may properly be fortified by addition of more alcohol. This may be repeated after two more passages, and thus a stronger vinegar (vinegar-sprit) is obtained.

REMOVAL OF ORGANIC MATTER FROM WATER

Sewage Treatment and Factory Effluents.—Almost any effluents from human dwellings or places of industry carry (as suspensions or in solution, or both) large amounts of organic waste material, which renders such discharges dangerous to higher life. With a better understanding of the life-cycles of microörganisms, these are now generally employed under controlled conditions for the purpose of decomposing and removing such waste matter, before allowing the waste-waters to pass into natural waterways.

This object is attained by permitting certain species of bacteria to invade the waste-waters and cause therein by their life-processes an attack upon and a destruction of any organic material present which they can utilize. These processes are identical with the processes, generally occurring in nature, called "putrefaction" which all serve the purpose of opening the way to a restoration to purposes of life all dead organic matter, by freeing the carbon contained therein, mainly as carbon dioxide (carbonic-acid gas) though sometimes hydrocarbons of the methane class may appear in a subordinate way.

The reduction of nitrates to nitrites and of sulphur in sulphates and albuminous material to hydrogen sulphide are frequently connected with the activity of microbes, among which the most powerful are the bacteria which liquefy gelatin, lactic- and butyric-acid bacilli, *bacillus coli*, bacilli *typhi* and particularly certain anaerobic species. Hydrolysis is caused by numerous bacteria and yeasts.

Cellulose is thus reduced by cytase to glucose, butyric acid or methane. An anaërobic bacillus, raised in pure culture by Omeliansky, decomposes cellulose into methane and carbon dioxide or hydrogen and carbon dioxide, with aldehyde and acetic acid as byproducts. Butyric acid is produced from almost any carbohydrates by *Bacillus butyricus* Hueppe, *Bacillus amylobacter* van Tieghem and *Clostridium butyricum* Prazsnowski. The corresponding decompositions of starch and sugars have been discussed in previous chapters.

Fats will give glycerin and free fatty acids by ferments called lipases. Urea is changed by urase, which has been found in over 60 species of bacteria, to ammonium carbonate; hippuric acid to benzoic acid and glycocoll. Albumes are reduced to albumoses and peptones by peptic and tryptic enzymes. Glycerin (when diluted, as is always the case in effluents) is fermented by many bacteria, yielding alcohol, acetic, formic, and succinic acids; or butyl alcohol and butyric acid. A great many more examples might be cited; but the above will suffice to show the complexity of the processes involved.

The essentials of a systematic plant for the purification of sewage consist, aside from the question of power for moving, of a sufficient number of tanks or, in large plants, basins, of which the first sets into which the sewage enters serve the purpose of settling out solid matter in suspension and to start the decomposition of organic matter present by fermentation, which may set in spontaneously or may be started by artificial infection with suitable material.

The end products of the fermentation are carbon dioxide and water, accompanied under certain conditions by methane and bad smelling gases of putrefaction. When this part of the process is finished, the liquid is transferred to other tanks or basins, where it is freed from any remaining obnoxious odors by aëration, there it passes usually through clarifying and settling tanks or basins, after which it is ready for discharge. There is no pure culture required for sewage treatment. The process can be initiated by ferments picked up from the air. The fermentation period in this case may last almost a year. It can be materially shortened by using material from a previously fermented tank, without any regard for "pure" cultures.

In conclusion it may be pointed out that fermentation should play an important part in the chemical industries of the future quite apart from the production of ethyl alcohol for industrial purposes or (in other countries) the old familiar arts of brewing and distilling. There seems to be no underlying reason why ethyl alcohol should be the sole fermentation alcohol produced on a large scale. *N*-propyl alcohol is among the fermentation products of fermenting starch with *Amylobacter butylicum* and *A. aethylicum*. Methyl alcohol is produced as one of the products of the fermenting of glycerol with the *Bacillus boocopricus*. There is an endless field for work with various ferments and various substrata for the production of all of the alcohols.

Suggestive of the lines along which fermentation processes may be extended is the way in which chemistry and bacteriology work together in glycerin production. Since glycerin can be produced by the reduction of glyceric anhydride and dioxyacetone, and since there is some reason for believing these substances are formed as intermediate products in the ordinary alcoholic fermentation, if one could add a strong reducing agent to alcoholic fermentation and still have the ferment function, it seemed logical that glycerin would be the product. Certain yeasts were found that would grow in the presence of large amounts of sodium sulphite and sodium bisulphite, and glycerin was produced by fermenting in this way. (Br. Pat. 163,034 of 1921.)

The methods given above for the production of pure cultures both on a small and on a large scale are entirely general. It is also a general proposition that up to a certain point warmth hastens fermentation, until a certain temperature is reached, the "optimum," and that as a rule, it is only a little above this point that the bacteria are killed by heat. On the other hand, intense cold, though it renders the bacteria inactive, usually does not kill. As a rule also, acids and alkalis are alike fatal to the fermenting organisms, and usually the end product of the fermentation is itself a poison to the bacteria causing it. Some bacteria require air for their proper growth, others require freedom from it (anaerobic). To some extent these means may be used partially to purify cultures.

Apart from the interesting problems of fermentation with microörganisms the chemist also has the practically untouched field of the extraction and use of the enzymes, that is, of chemical fermentation

SECTION XVIII

FRACTIONAL DISTILLATION

By W. F Faragher[1]

The Field of Distillation.—It is frequently desirable to separate naturally occurring mixtures, or those prepared by laboratory or factory processes, into their components. The extent of the separation required may vary from a slight enrichment of the products in one or several of the components, to the isolation, with maximum yield, of each constituent in a state of practical purity. In the event that the mixture is a liquid, the method of separation which is most frequently effective and which is, therefore, most frequently applied is fractional distillation.

The purpose of fractional distillation as given in substance above, is quite distinct from that of simple distillation as exemplified in the preparation of distilled water, and also from that of drying, as illustrated by the evaporation of water from soap or glue, or of organic solvents from films of nitrocellulose or cellulose acetate. The last two processes are closely akin in aim to the concentration of solutions of practically non-volatile substances and are discussed in Section IX. The removal of volatile constituents as a whole characterizes these processes and any separations or changes in the concentrations of the liquids which occur are only incidental. Provisions are of course made for the recovery of expensive solvents. However, the objects in view are obviously distinct from those of fractional distillation.

In a given fractionation, the results obtained are controlled by the number of successive distillations carried out and by the character of the apparatus used. Industrial equipment has been brought to a high state of efficiency as a result of the pressure of commercial demands. Empiricism has necessarily had a large part in this development, but an increasing insight into the processes which occur has been of inestimable value. The basis of the latter factor is found in the numerous investigations of the laws which govern the changes of vapor-pressures of mixtures of liquids with changes of temperature, pressure and composition of the liquid. The abolition of empiricism awaits the formulation of generally applicable quantitative laws.

Vapor-Pressure.—If a pure substance is introduced in successive small quantities into an evacuated vessel which is maintained at a constant temperature, it is found, in general, that certain of the first portions change completely into vapor. After the evaporation of each portion, the vapor exerts a definite pressure upon the walls of the vessel. The actual values of these pressures for a given substance (so long as the liquid evaporates completely) depend only upon the total mass of the substance which has been introduced and upon the volume of the vessel. As the concentration of the vapor increases, the pressure in the vessel increases in approximate agreement with the general gas law. Experimentally it is found that the concentration and therefore the pressure of the vapor can not be increased indefinitely under the conditions stated above. After the pressure reaches a certain value, the introduction of more liquid effects

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no further increase of pressure. In fact, the liquid remains unchanged and even effects the condensation of some of the vapor. Otherwise the vapor, occupying a smaller volume, would exert a higher pressure. ($p_1v_1 = p_2v_2$, and $p_2 > p_1$, since $v_1 > v_2$. p_1 and v_1 represent the pressure and the volume respectively before the liquid was present as such, p_1 having its maximum value; and p_2 and v_2 represent the values of the pressure and volume which would obtain if there were no condensation of vapor after liquid accumulated in the system. By thus excluding the possibility of the condensation of vapor and the further evaporation of liquid, the mass of the vapor would remain constant, and Gay-Lussac's law should hold as presented.) As more and more liquid is added to the vessel, the volume of liquid increases and that of the vapor decreases. The pressure exerted by the vapor, however, remains constant. Liquid and vapor are in equilibrium, then, when the vapor exerts a certain pressure which is called the vapor-pressure (or vapor-tension) of the substance. When the volume of the liquid placed into the vessel just equals the volume of the vessel, the vapor phase is lacking.[1] Any further addition of liquid increases the pressure in the vessel very greatly on account of the low compressibility of liquids.

At any other temperature than that of the above considerations, analogous conditions are observed. At each temperature a pure substance and its vapor can exist in equilibrium only at one fixed pressure (dissociations, pressure due to other vapors or gases, etc., are excluded). Increase of vapor-pressure always accompanies a rise in temperature.

The vapor-pressure of a pure substance is a function of the temperature, and is independent of the relative or absolute volumes of the liquid and vapor phases. On the other hand, we may regard the pressure as the independent variable, and the temperature as the dependent variable. For a given substance, kept at a definite pressure, p_1, liquid and vapor can coexist unchanged only at one fixed temperature, T. At higher temperatures, the liquid changes wholly to vapor, and at lower temperatures the vapor condenses more and more to liquid.

The case is covered fully by the phase rule, as it is ordinarily stated: $P + F = C + 2$. (P = number of phases in the system; F = number of degrees of freedom; and C = number of components of the system.) For a system having the two phases, pure liquid and its vapor, we may make one choice of the variables, pressure and temperature, which determine the condition of the system. The other variable then assumes a fixed value.

In dealing with a fixed mass of a pure substance, we find that we may choose either the temperature and the total volume or the pressure and the total volume, at which liquid and vapor shall coexist. The total volume, however, may vary only from v_1, the volume which the given mass of the substance occupies as liquid, to v_2, the volume which it occupies as saturated vapor at the temperature and pressure which exist. We cannot, however, choose both the temperature and the pressure under these conditions.

It is not essential that we consider the vessel, in which equilibrium between liquid and vapor is established, to be evacuated. It may contain any indifferent gas at any pressure, p, up to quite considerable values, without influencing greatly the value of the pressure of the vapor at equilibrium. In this connection, an indifferent gas is one which is not appreciably soluble in the liquid and which does not react chemically with it. The chief difference in the two cases is the length of time required for the

[1] Strictly speaking, this volume is measured at the temperature of the vessel and at the pressure of the saturated vapor.

establishment of equilibrium. In the first case, the vapor from the liquid very quickly fills the whole free space, while in the second case it must diffuse slowly through the relatively highly concentrated, indifferent gas. The behavior of mixed vapor and indifferent gas, as outlined above, is in agreement with Dalton's law of partial pressures; $P = p_1 + p_2$. P is the total pressure in the vessel; p_1 is the partial pressure of the vapor (the vapor-pressure of the substance); and p_2 is the partial pressure of the indifferent gas. For the establishment of equilibrium between liquid and vapor, only p_1 is of consequence.

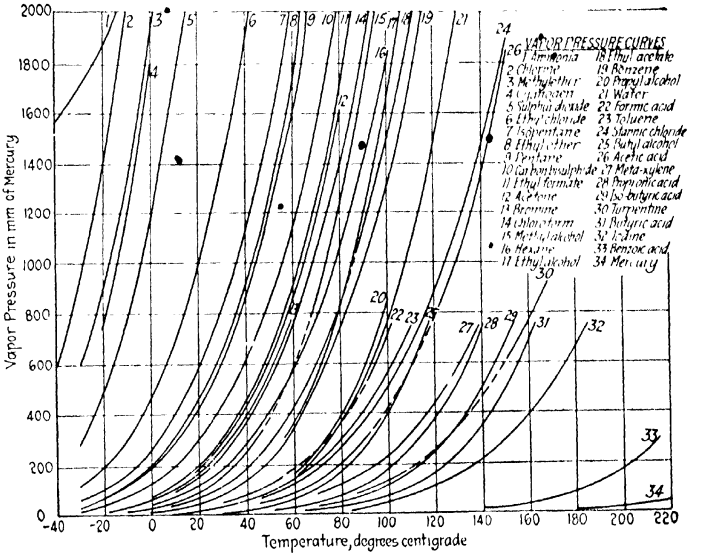


FIG. 1.—Vapor-pressure curves of various substances

The form of the vapor-pressure-temperature curve is approximately the same for all pure substances. With rising temperatures, the vapor-pressure increases relatively quite rapidly, suggesting an exponential relationship between the variables. Curves for various substances are shown in Fig. 1.

In the above discussion of vapor-pressure, we have stipulated that the vessel and its contents are kept at a constant temperature, while a given vapor-pressure is being realized. The evaporation of the required mass of liquid is effected, obviously, by the absorption of heat from the surroundings. In order to convert one mole[1] of the substance into saturated vapor (at the conditions of the system), a quantity of heat equal to the molar heat of evaporation of the substance must be added. Likewise, the reverse change, when effected, is accompanied by an evolution of heat, the molar heat of condensation. These two heat quantities are equal numerically. The spontaneous establishment of equilibrium between vapor and liquid is controlled by these energy relationships.

The behavior of the system in equilibrium, with changes of temperature or pressure, is predicted by the Le Chatelier-van't Hoff law of mobile equilibrium. For example, the addition of heat to the system, which tends to raise the temperature,

[1] A mole (or gram-molecule) of a substance is the weight in grams of the substance equal to its molecular weight, thus, a mole of water would be 18 grams ($H_2 + O = 2 + 16$).

is followed by the evaporation of additional liquid, a reaction which absorbs heat. There is produced, as a net result, an increased partial pressure of the vapor at the resulting higher temperature.

Form of the Vapor-Pressure Curve.—If the corresponding values of vapor-pressure and temperature are plotted in a system of rectangular coordinates, the former being ordinates and the latter abscissas, a curve which grows increasingly convex toward the axis of abscissas as the temperature rises is generally obtained for pure substances. Since just above the critical point liquid can no longer exist, the vapor-pressure curve must end there. For a pure liquid, the curve may be considered to end at the freezing-point. However, in many cases the curve is experimentally realizable at lower temperatures. At these temperatures, the liquid is supercooled and the curve obtained is found to be a continuation of the curve for the substance at temperatures above the freezing-point. While the vapor-pressures of the liquid and the solid phases of a substance are equal at the freezing-(or melting-) point, as is required by the phase rule, the vapor-pressure curve of the solid phase, at lower temperatures, lies below the continuation of the vapor-pressure curve of the liquid. This behavior is to be expected, since at all of these temperatures the supercooled liquid is unstable with respect to the solid phase. The unstable form has the higher vapor-pressure, and the continuation of the vapor-pressure curve of the liquid is simply the vapor-pressure curve of the supercooled liquid. The lower limit of the vapor-pressure curve of a substance may, perhaps, be considered to lie at the absolute zero, where vapors are theoretically incapable of existence.

The vapor-pressure curve as described above is also the boiling-point curve of the substance. This statement follows from the fact that if the external pressure is made equal to the vapor-pressure of the substance, p, at the corresponding temperature, T, the substance will boil. In the same way, the vapor-pressure curve of a solid substance is its sublimation curve.

Many attempts have been made to formulate a general law which will express with the required accuracy, the relationship between vapor-pressure and temperature for pure substances. Theoretically, the solution of the problem is given by the Clausius-Clapeyron equation. This equation relates the heat of evaporation of the liquid, the temperature, the specific volumes of the vapor and of the liquid, and the temperature coefficient of the vapor-pressure. The derivation of this equation is accomplished by utilizing the first two laws of thermodynamics.

Consider a mole of the substance to be contained in a cylinder fitted with a frictionless, weightless piston, which is contained in a reservoir of constant temperature, T. The piston rests upon the liquid, and is loaded with weights so that the pressure on the liquid is equal to the vapor-pressure, p, of the substance. The volume of the liquid, v_1, is the molar volume at the existing temperature and pressure. The whole of the liquid is caused to evaporate reversibly and isothermally, by slowly drawing out the piston. The final volume, v_2, is the molar volume of the saturated vapor. During the evaporation, a quantity of heat, L_v, which is the molar heat of evaporation, passes from the reservoir to the contents of the cylinder and the vapor performs the external work $W_1 = p(v_2 - v_1)$.

This change is represented by the line AB in Fig. 2. The mole of saturated vapor is then allowed to undergo an adiabatic expansion, until the pressure reaches a value $p - dp$, which corresponds to the vapor-pressure of the substance at a temperature $T - dT$. In the absence of the liquid phase, this change is considered to occur with no condensation of vapor. Graphically, the expansion is represented by the

curve BC. During this change, the volume increases to $v_2 + dv_2$, and the temperature falls to $T - dT_1$, which may be higher or lower than $T - dT$, the equilibrium temperature for the pressure $p - dp$. The work performed by the gas during this adiabatic expansion is $W_2 = (p - dp)dv_2$, or neglecting the product of the two differentials, $W_2 = pdv_2$. At the constant pressure $p - dp$, the gas is then brought from the temperature $T - dT_1$ to the equilibrium temperature, $T - dT$. If $dT_1 > dT$, the vapor must be raised in temperature by the addition of heat, and if $dT_1 < dT$ heat must be abstracted from the vapor. The quantity of this heat is given by the equation $Q = C(dT - dT_1)$. C is the molar specific heat of the vapor under the existing conditions. A further amount of work, W_3, is done during this adjustment of temperature,

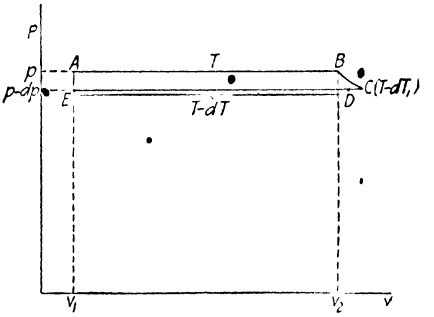


FIG. 2.—Curve illustrating Clausius-Clapeyron equation.

and its value is $(p - dp)dv_3$, where dv_3 is the volume change which occurs. In the diagram, this change is represented by the line CD. Since the volume change shown is negative, heat was removed from the vapor, and dT_1 was less than dT. The conditions represented at D are those of the saturated vapor at the temperature $T - dT$ and under the pressure $p - dp$. By condensing the vapor reversibly at this temperature, the changes pictured by the line DE are effected. The work done upon the vapor, W_4, is equal to $(p - dp)(v_2 + dv_2 - dv_3 - v_1)$. Also, heat to the value of the molar heat of condensation under these conditions, $L_v + dL_v$, is given up to the surroundings. Any change of molar volume of the liquid, v_1, caused by the change of temperature, dT, is regarded to be negligible in comparison with the change in the molar volume of the vapor.

After the condensation of the vapor is complete (point E), the liquid is restored to its original conditions of temperature and pressure by the addition of heat. The quantity of heat required is $Q_1 = C_1 dT$, where C_1 is the molar specific heat of the liquid. Regarding the work done by the vapor as positive, and that done upon it as negative, the whole of the work gained is

$$\begin{aligned} dW &= W_1 + W_2 - W_3 - W_4 \\ &= p(v_2 - v_1) + pdv_2 - (p - dp)dv_3 - (p - dp)(v_2 + dv_2 - dv_3 - v_1) \\ &= (v_2 - v_1)dp, \text{ if the products of differentials are disregarded.} \end{aligned}$$

Since, in the limiting case, the process has been conducted reversibly and the system restored to its original condition, the essential feature consists in the transfer of L_v heat units from the temperature T to the temperature $T - dT$. We know, therefore, that the second law of thermodynamics is applicable.

$$dW = Q \cdot \frac{dT}{T} = L_v \cdot \frac{dT}{T} = dp(v_2 - v_1).$$

or

$$\frac{dp}{dT} = \frac{L_v}{T(v_2 - v_1)}$$

This is the equation known as the Clausius-Clapeyron equation.

If the molar heat of evaporation and the specific volume of the liquid are known as functions of the temperature, and if, further, the molar volume of the vapor can be calculated accurately from the temperature and the pressure by using a suitable equation of state, the changes of vapor pressure with changes in temperature can be calculated with great accuracy. However, data which are sufficiently extensive and accurate for this purpose are not generally available.

At temperatures and pressures not too close to the critical values, the molar volume of the liquid is negligible in comparison with that of the vapor. The equation then assumes the simple form:

$$\frac{dp}{dT} = \frac{L_v}{Tv}$$

By assuming that the gas laws are applicable to the vapor, the substitution of RT/p for v may be made in the above equation.

$$dp/dT = L_v p/RT^2, \text{ or } d \log p/dT = L_v/RT^2$$

Before this equation can be integrated, the molar heat of evaporation, L_v, must be expressed as a function of the temperature, T. For temperatures not too widely separated, L_v may be regarded as constant, and in this form the equation is frequently useful.

Integrated between the pressures p_1 and p_2, corresponding to the temperatures T_1 and T_2 (T_1 being the higher temperature), the solution is as follows:

$$\log p_1 - \log p_2 = \frac{L_v}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

By changing to Briggsian logarithms and substituting the value of R in calories, we get the form:

$$\log_{10}\left(\frac{p_1}{p_2}\right) = \frac{L_v}{1\,985 \times 2.303}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Many of the most important equations which have been proposed and tested for calculating the observed vapor-pressure curves of various substances, are reducible to an equation derived from the above. In the derived equations, the dependence of L_v upon the temperature is calculated thermodynamically in terms of the molar specific heats of the liquid and of the vapor. The molar volume of the vapor is expressed by one of the equations of state.

Measurement of the Vapor-Pressure of a Pure Substance.—There are two general methods for measuring the vapor-pressures of substances: the static and the dynamic methods. In the former method after equilibrium has been established between liquid (or solid) and vapor, the relative volumes of the phases remain constant. In the various dynamic methods, on the other hand, the relative volumes change steadily. The limitations and advantages of the different methods are discussed in the standard guides for making physico-chemical measurements.

A suitable method for measuring the vapor-pressures of substances at temperatures lower than their normal boiling-points, has been devised by Ramsay and Young (*Phil. Trans.*, Series A, Vol. **178**, p. 57 (1887); also "Stoichiometry," Sydney Young, p. 121, Longmans, Green & Co., London, 1918). The apparatus is shown in Fig. 3. The tube on the left is a simple barometer, which is provided with a jacket so that it may

be kept at a known constant temperature by a stream of water. On the right is a barometer tube of special form, which is also jacketed in order to maintain the tube and its contents at any constant temperature by means of the saturated vapor of a suitable liquid which is boiled at the requisite pressure. Some of the liquid to be investigated is introduced into the tube on the right (details, *l.c.*) and after equilibrium has been established, the vapor-pressure is read. It is necessary to reduce both of the columns of mercury to their values at 0°C., and to take into account the effect of the small column of unevaporated substance.

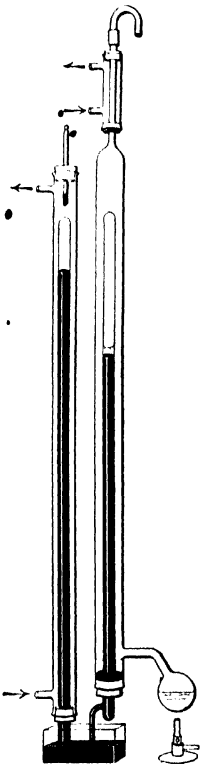


FIG. 3—Vapor-pressure apparatus

Two very useful methods have been developed by Alexander Smith and A. W. C. Menzies. The first of these is a static method[1] and the second a dynamic method.[2] The principle of a large number of dynamic methods which have been proposed is the determination of the boiling point of the substance at a series of pressures. The method of Smith and Menzies and that of Ramsay and Young[3] are representative, and both give accurate results.

For substances which have relatively low vapor-pressures at the temperatures employed, methods based upon one proposed by James Walker[4] are useful. A current of an indifferent gas at a known pressure and the desired temperature is passed over or through the substance. Precautions are necessary to insure that the gas-stream leaves the substance at the equilibrium temperature and that the partial pressure of the substance reaches the value of its vapor-pressure. Measurements of the volume of the indifferent gas, the total pressure, the temperature and the weight of substance which has evaporated, provide the data which are necessary for the calculation of the vapor pressure. In the calculation, it is assumed that the vapor of the substance obeys the gas laws, and that the formula of the substance as vapor, *i.e.*, its molar weight, is known.

Dependence of Vapor-Pressure upon the Total Pressure upon the Liquid.—In our discussion of the vapor-pressure of a pure substance, we have so far disregarded the effect of the total pressure exerted upon the liquid. The applicability of Dalton's law of partial pressures was, however, expressly limited to moderate total pressures, and might well have been limited to temperatures considerably distant from the critical temperature.

That the vapor-pressure does depend upon the total pressure borne by the liquid, may be shown by a simple thermodynamic calculation.[5] The equation which expresses the relationship is as follows:

$$\left(\frac{dp}{dP}\right)_T = \frac{v_0}{V_0}$$

[1] *Jour. Am. Chem Soc*, Vol **32**, pp 1412-34

[2] *Jour Am Chem. Soc*, Vol **32**, pp. 897-905, 907-14 and 1448-59 (1910)

[3] *Phil. Trans*, Vol. **175**, p. 37 (1884), also "Stoichiometry," SYDNEY YOUNG, p 129.

[4] *Zeit. phys. Chem.*, Vol. **2**, p. 602 (1888).

[5] WASHBURN, "Principles of Physical Chemistry" McGraw-Hill, New York, 1915, p. 409.

At any constant temperature, T, therefore, the rate at which the vapor-pressure, p, increases with an increase of the pressure P, upon the liquid, is equal to the molar volume of the substance as liquid v_0, divided by the molar volume as saturated vapor, V_0. Both molar volumes are, of course, to be measured under the conditions which exist in the system. Analogous considerations give similar relationships between the partial vapor pressures of substances in solution and their corresponding molar volumes as liquid and vapor. In this case, both the mole fraction, n, and the temperature are considered to be constant. The partial molar volume as liquid, $v_{0,A}$ is the increase in volume which is produced by adding one mole of substance to a very large volume of the given solution.

The equation has the form:

$$\left(\frac{dp_A}{dP}\right)_{T,n} = \frac{v_{0,A}}{V_{0,A}}$$

At temperatures which are sufficiently far removed from the critical temperature, it is obvious that change of vapor-pressure is not great for moderate changes of P (v_0 [and $v_{0,A}$] is small in comparison with V_0 [or $V_{0,A}$]). With rising temperatures, however, the ratio of the specific volumes increases, becoming unity at the critical temperature.

Dependence of Vapor-Pressure upon the Form of the Liquid Surface.—In the methods of experimentation assumed in the previous discussion of vapor-pressure, as well as in the methods described for measuring vapor-pressure, the liquid surface is either plane, or has a large radius of curvature. Under these conditions, the form of the surface influences only very slightly the value of the vapor-pressure at a given temperature. It has been shown by Lord Kelvin,[1] however, that the curvature of the liquid surface can not be neglected if the radius of curvature is very small. The vapor-pressure of a substance with a concave surface is smaller, and that of the substance with a convex surface is greater than the vapor-pressure of the substance with a plane surface. These considerations are of moment in the event that the liquid is present in the form of small droplets or of films.

Vapor-Pressure of Mixed Liquids.—Pairs of liquids show varying behaviors when they are mixed. In some cases, there is practically zero solubility of the liquids in each other, while in other cases the solubilities are limited. On the other hand, many pairs of liquids mix in all proportions, the process of solution being accompanied, as a rule, by contraction or expansion in volume, and by the evolution or absorption of heat. Pairs of liquids which are related chemically, such as bromobenzene and chlorobenzene, form solutions without undergoing appreciable changes in total volume and in temperature.

These differences in behavior may be pictured in terms of the attractions of the like molecules of each liquid for one another, and of the attractions of the unlike molecules of the two liquids for each other. In the event that the former attractions are relatively large, the two liquids should show little or no tendency to form solutions. A pair of liquids for which the attraction of the unlike molecules is relatively greater, should be more miscible. Still other pairs of liquids with progressively larger values of the attractions of the unlike molecules should be progressively more miscible, reaching finally the condition of complete miscibility. In the case of the partially miscible liquids, there should be, in general, an increase in the total volume. The considerations for this conclusion are that strong attractions of like molecules, which cause, supposedly, relatively small volumes, give way in part to weaker attractions with their accompanying larger volumes. With increasing miscibility, this expansion

[1] *Phil. Mag.* (4), Vol. **42**, p. 448 (1871).

upon mixing should become smaller, then disappear, and eventually be followed by contraction in the total volume. In the formation of the dilute solutions of partly miscible liquids, there should be absorption of heat, which should grow smaller and finally change to an evolution of heat as the tendency to exhibit complete miscibility increased. The reason for this behavior is the assumption that the work necessary to overcome the relatively strong attractions of the like molecules is greater than that gained when the weaker attractions of the unlike molecules are satisfied. Although the changes outlined above are in general in harmony with experimental data, exceptions in the case of completely miscible liquids are of frequent occurrence. For example, the addition of propyl alcohol to water is at first accompanied by a contraction in the total volume and an absorption of heat. Pairs of liquids which are closely related chemically, probably have attractions between all of the molecules which are approximately equal. Daniel Berthelot[1] and also Galitzine[2] have proposed that in these cases, the following relationship holds: $A_{1,2} = \sqrt{A_1 A_2}$. $A_{1,2}$ represents the attraction of the unlike molecules, and A_1 and A_2 the attractions of the like molecules of the two liquids, A_1 and A_2 respectively.

An explanation of the volume changes on the basis of molecular attractions as outlined above was suggested by Brown in 1881.[3] If the attractions of the like molecules exceeded those of the unlike, the mean attraction should be decreased upon the formation of a solution. In keeping with this change, the volume of the solution should exceed the sum of the volumes of the liquids. Brown added the objection, however, that in view of this decrease in the value of the mean attraction, it would be difficult to understand why the solution should be formed at all.

More recently these ideas have been given definiteness by Washburn[4] in his presentation of the conception of thermodynamic environment. Two liquids which are as unlike chemically as mercury and benzene separate quickly into two layers after they are shaken together. Each layer is practically a pure substance, since analytical methods are not sufficiently accurate to detect the presence of a second substance in either case. If the mercury is replaced by water, which does not resemble benzene closely, but which is much more like benzene than is mercury, we find that each substance, at a given temperature, dissolves slightly in the other. At ordinary temperatures, the benzene layer contains about 0.03 per cent of water, and the water layer about 0.01 per cent of benzene. In order to have benzene soluble in all proportions in a second liquid, it is necessary to choose a liquid which is still more like it chemically. Ordinary alcohol is such a liquid. The attractive forces between the different molecules are such that whatever the proportions in which they are present, the molecules can accommodate themselves to the conditions which exist. The first portions of alcohol which are added are in an environment essentially like that in pure benzene. With increasing quantities of alcohol, the conditions in the solution differ less and less from those in pure alcohol. Finally, the conditions approximate those in pure alcohol.

The tendency for a given molecule of any substance to leave a solution is determined by the conditions which exist in the solution. The sum total of all of these conditions in respect to a given molecular species, constitute the thermodynamic environment for that species. Some of these factors are the attractive and repulsive forces of the molecules, and the effects resulting from the collisions of molecules. The mole fractions and the natures of the substances constituting the solution, as well as the temperature and the pressure, influence the thermodynamic environment.

The thermodynamic environment in mercury and even that in water, is so different

[1] *Compt. rend.*, Vol **126**, p. 1703 (1898).
[2] *Wied. annalen*, Vol **41**, p. 770 (1890).
[3] *Jour. Chem. Soc.*, London, Vol. **39**, p. 212.
[4] *Lib. cit.*, p. 134.

from the thermodynamic environment in benzene, that solutions of appreciable concentrations cannot be formed. Alcohol and benzene are not closely alike, but their differences are not so great that the molecules of either are unable to enter into the conditions existing in the solutions of both. That differences exist, however, is indicated by the appreciable fall in temperature which occurs when equal molar quantities of the two substances are mixed. (The volume change is negligible.)

In the formation of solutions of two substances, two opposite tendencies develop with increasing concentrations of one of them, *e.g.*, the solute. At very low concentrations, the attractive forces of the molecules of the solute scarcely come into play, since these molecules are separated by relatively great distances. As the concentration increases, the forces become of importance, and may cause the molecules of the solute to form a separate phase of more suitable thermodynamic environment. At the same time, however, the opposite tendency develops, and may act as a check to such a separation: with increasing concentration, the condition of the solution surrounding any molecule of the solute becomes more like that in the pure solute. The tendency for the solute to separate as a separate phase is consequently smaller.

In general, even those substances which are wholly miscible, differ so much in their thermodynamic environments that the change to the new conditions in a solution is accompanied by appreciable changes in volume and energy content. Non-associated liquids which undergo no chemical reactions upon mixing may be considered to indicate roughly the magnitude of their differences of condition by the amount of the changes in volume and in energy content.

The importance of the internal pressures of non-polar[1] liquids in relation to their escaping tendencies from solutions, has been emphasized by Hildebrand.[2] As measured by the closeness with which Raoult's law is followed, Hildebrand has shown that in some cases, approximate equality of internal pressures is of more importance than chemical similarity.

Vapor-Pressures of Non-miscible Liquids.—A mixed vapor from two or more liquids which are practically insoluble in one another follows Dalton's law of partial pressures: The vapor from each liquid behaves approximately as if it were alone in the vapor-space. It follows, therefore, that the boiling-point of a mixture of such liquids is lower than that of any of the single liquids. These facts were recognized by Gay-Lussac,[3] and were proved experimentally by Régnault.[4] Since the partial pressure of each liquid remains constant during the distillation of such a mixture it is possible to calculate the relative weights of the liquids obtained in the distillate.

Let P_A and P_B represent the partial pressures of the two liquids, A and B, in the mixture which is boiling at the temperature t. The molar weights of the liquids in the vapor form are M_A and M_B. In each liter of mixed vapor, there is one liter of A at a pressure P_A and temperature t, and one liter of B at a pressure P_B and temperature t. The volume of each substance as vapor corrected to normal conditions and expressed in liters is as follows, assuming that the gas laws are applicable:

$$\text{For } A,\ V_{0,A} = \frac{273 \times P_A \times 1}{(273 + t) \times 760}$$

$$\text{and for } B,\ V_{0,B} = \frac{273 \times P_B \times 1}{(273 + t) \times 760}$$

[1] See p. 621.

[2] *Jour. Am Chem Soc.*, Vol. **38**, p. 1452 (1916); *ibid*, Vol. **39**, p 2297 (1917); and *ibid.*, Vol. **41**, p. 1067 (1919).

[3] *Ann. Chim Phys.* (I), Vol. **49**, p. 393 (1832), *Pogg. Ann* Vol **25**, p 498 (1832).

[4] *Mém. de l'Académie de l'Institut de France*, Vol. **26**, p. 715 (1862).

The weight of each of these corrected volumes of vapor is obtainable from the relation that one mole of a substance as vapor at normal conditions occupies a volume of 22.4 liters.

$$\text{Weight of } A\text{: } W_A = \frac{273 \times P_A \times 1 \times M_A}{(273 + t) \times 760 \times 22\ 4}$$

$$\text{Weight of } B\text{: } W_B = \frac{273 \times P_B \times 1 \times M_B}{(273 + t) \times 760 \times 22\ 4}$$

The relative weights are, then:

$$\frac{W_A}{W_B} = \frac{P_A\ M_A}{P_B\ M_B}$$

In an experiment described by Young,[1] 80 g. of water and 110 g. of chlorobenzene were distilled at a pressure of 740 2 mm. The temperature varied only from 90.25° to 90.35° while practically all of the chlorobenzene was distilling. The temperature then rose rapidly to nearly 100°. The distillate was collected in five fractions, the average composition being 71 4 per cent chlorobenzene. The percentage calculated from the above formula is 71.2 per cent chlorobenzene.

In a distillation of a mixture of aniline and water, which dissolve one another relatively more than the above pair of liquids, the composition of the distillate was found to be independent of the relative weights of the two liquids The percentage of aniline in the distillate, however, was appreciably lower than that indicated by the formula. This fact is not surprising, since the partial pressure of each liquid, considered as a solvent, is lowered by the other substance, the solute, and the partial vapor pressures from the solution are not necessarily in the same proportion as the vapor pressures of the pure liquids at the same temperature

The theory of the steam-distillation of pure organic liquids which are not very soluble in water, is outlined in the above discussion For the process to be utilizable in a given instance, the organic substance must be stable towards water at the temperature of distillation, which is usually only slightly below that of water, but considerably below that of the pure organic substance. The relative weight of the organic substance in the distillate may be satisfactory even for high-boiling substances, since the unfavorable effect of low partial pressure of the organic compound is offset by the relatively large value of its molar weight in the vapor form

Miscible Liquids.—The lowering of the vapor-pressure of a substance by the addition of some of another substance which yields a solution is predictable from the van't Hoff-Le Chatelier law of mobile equilibrium. The condensation of some of the vapor above the solution dilutes the solution which was formed, and results in a condition which is more like that in the original pure liquid. The more dilute vapor of the original substance which remains above the solution possesses a smaller pressure than the vapor-pressure of the pure liquid. If the added liquid has an appreciable vapor-pressure at the temperature of the solution, the vapor in equilibrium with the solution will be mixed and the total pressure will be made up of the partial pressures of the two constituents. The partial pressure of the added constituent will be less than the vapor-pressure of that liquid at the same temperature, since the relationships of solvent and solute are reciprocal.

The behavior of pairs of non-electrolytic liquids, which are completely miscible, with regard to the total pressure of the equilibrium vapor, is illustrated by the three curves in Fig. 4. These curves apply at a constant temperature.

[1] "Fractional Distillation," SYDNEY YOUNG, MacMillan, 1903, p. 90.

The compositions of the solutions, expressed in mole fractions, are given on the axis AB, and the total pressure of the mixed vapors by the perpendicular distances from the curves to the axis AB. Experimentally, curves of these three types have been realized.

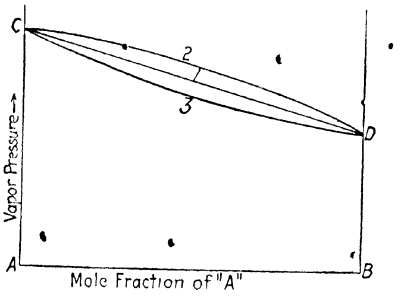


FIG. 4.—Total pressure curves.

In Fig. 5, three experimentally determined types of partial-pressure curves[1] of completely miscible, non-electrolytic pairs of liquids are shown.

In the simplest type of total pressure curve, 1, (Fig. 4) the pressure rises in direct proportion to the mole fraction of the more volatile constituent, A. The pressure for

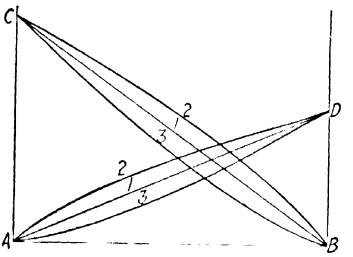


FIG. 5.—Partial pressure curves.

a mixture of given composition is, therefore, expressed by the following formula:

$$P = \frac{P_A m_A + P_B(100 - m_A)}{100}$$

P is the total pressure, P_A and P_B the partial pressures of pure A and pure B, respectively, at the same temperature as that of the solution, and m_A is the mole fraction of A in the mixture.

For those liquids which yield curves of type 2, the total pressure rises more rapidly than the mole fraction of A. The total pressure of liquids which furnish a curve of type 3 increases more slowly than the mole fraction of A.

Similar considerations hold for the partial pressure curves of Fig. 5. According to the summary presented by Kuenen[2] about 160 pairs of liquids (non-electrolytes) have been examined carefully. Of these, only about 10 per cent give curves of the simple type 1. Of the remainder, about 10 per cent have curves of type 3, and the other 80 per cent, therefore, correspond to type 2.

[1] *Zeit. phys. Chem.*, **64**, 727

[2] "Theorie der Verdampfung und Verflüssigung von Gemischen" "Bredig's Handbuch, No. 4. Leipsig, 1906, p. 133.

The general equations which express the relationships between the changes of the partial pressures of the vapors of the constituents in a binary solution are as follows:

$$\text{For } A, \frac{dp_A}{dn_A} = f_A(T, E) \text{ and for } B, \frac{dp_B}{dn_B} = f_B(T, E)$$

These equations express the conditions where the mole fractions are changed from n_A and n_B to $n_A + dn_A$ and $n_B + dn_B$, respectively.[1] The corresponding pressure changes are from p_A to $p_A + dp_A$ and from p_B to $p_B + dp_B$. The right-hand members of the equations show that the ratios of the small changes of partial pressures to the small changes of the mole fractions are functions of the thermodynamic environment (T, E.) in the solution. The temperature and the total pressure are considered to remain constant during these changes.

In order to utilize the equations, *i. e.*, to integrate them, it is necessary to know the form of the functions on the right-hand side of the equations. No general formulation which is applicable to all kinds of solutions has yet been made.

A limited number of solutions have thermodynamic environments which remain practically constant for varying constitutions. For these solutions the above equations assume a form which can be integrated directly:

$$\frac{dp_A}{dn_A} = k_A, \text{ and } \frac{dp_B}{dn_B} = k_B$$

The integrated equations are as follows:

$$p_A = k_A n_A + C_A, \text{ and } p_B = k_B n_B + C_B$$

The constants of integration, C_A and C_B, are seen to be equal to zero, since when n_A or n_B is zero, the partial pressure p_A or p_B, respectively, is zero, as is also the corresponding constant of integration.

The significance of the proportionality factors, k_A and k_B, is shown by making n_A and n_B equal to unity. The partial pressures p_A and p_B then equal the vapor-pressures of the pure substances A and B, respectively. The equations for such solutions, which are called ideal solutions, assume the following forms:

$$p_A = p_{o,A} n_A \text{ and } p_B = p_{o,B} n_B$$

In these equations $p_{o,A}$ is the vapor-pressure of pure A, and $p_{o,B}$ that of pure B at the temperature of the solution. If we consider the substance A as the solvent, the equation $p_A = p_{o,A} n_A$ is simply a statement of Raoult's law in its simplest form. In the same way, considering B as the solute the equation $p_B = p_{o,B} n_B$ is really a slightly modified form of Henry's law. It has been shown by Lewis[2] that if vapors obey the gas laws, the law of Henry may be derived by thermodynamic considerations from Raoult's law. The former law, therefore, must hold for solutions which follow the latter law. There can be no question that the most satisfactory criterion of an ideal or perfect solution is agreement with Raoult's law.

In binary solutions of liquids in general, Raoult's law expresses the existing relationships when the mole fraction of the one constituent is quite large in comparison with that of the other constituent. This statement is equivalent to saying that in dilute solutions Raoult's law is valid. The curves of types 2 and 3 (Fig. 5), then, tend to become tangent to curve 1 at the extreme concentrations, as shown.

Two general methods of explaining the causes of the deviations from Raoult's law have been advanced. In the one, supported in particular by Dolezalek,[3] a chemical reaction between the two constituents, or the formation of complex molecular species of one or both of the constituents, is considered to occur. Raoult's law, however, is

[1] WASHBURN, *Lib. cit.*, pp. 132 and 143.

[2] *Jour. Am. Chem. Soc.*, Vol. **38**, p. 674.

[3] *Zeit. phys. Chem.*, Vol. **64**, p. 727 (1908), Vol. **71**, p. 191 (1910), Vol. **83**, p. 40 (1913).

still considered to hold for each molecular species in the solution. By an application of the law of mass action, Dolezalek has utilized this method in studying a number of systems which have been investigated. He has succeeded in obtaining calculated values which agree satisfactorily with the measured values.[1] In many cases, the requirements of the method are in accordance with the general characteristics and behavior of the substances. In other cases, however, the interpretations require chemical reactions or associations which are at variance with the commonly accepted nature of the constituents. For example, pairs of liquids which by all commonly recognized tests are normal, *i.e.*, non-associated, often have vapor-pressures in excess of those required by Raoult's law. According to Dolezalek, one of these liquids would have to be considered to be associated in the solution. In many cases, the degree of association indicated by the calculation is so great as to assign the substance definitely to the class of associated liquids. Such pairs of liquids are represented by bromine and carbon tetrachloride, carbon disulphide and methylol, benzene and hexane, and benzene and ether. The pair of normal liquids, hexane and aniline, have been found by Hildebrand and Keyes to deviate from Raoult's law to the extent of forming two phases at temperatures below 59.3°C.[2] An explanation of this behavior on the basis of association of the constituents, so that Raoult's law is applicable, is difficult to conceive.

The second method of explaining deviations from Raoult's law, is that suggested by van der Waals,[3] and adopted by van Laar[3] and Kohnstamm.[4] This theory relates the deviations from the law of Raoult to the constants of a modified van der Waals' equation, which is applicable to pairs of completely miscible liquids. The possible types of vapor-pressure curves are also predicted from the properties of the equation. For example, van Laar shows that we should expect a deviation from Raoult's law in the case of normal liquids, if their critical pressures are different. The method of van der Waals fails when one of the constituents is associated. Although the critical pressures may be practically the same, deviations from Raoult's law to the extent of the formation of two liquid layers may occur.

Raoult's law has a very simple kinetic basis. If the vapor of a binary mixture follows the gas law, and if the solutions have a practically constant thermodynamic environment, it is a natural conclusion that since only a fraction of the total number of molecules is that of one constituent, the partial pressure of that constituent should be less than the vapor-pressure of the pure substance. Since the fraction of the total number of molecules is expressed by the mole fraction of the constituent, it is to be expected that the partial pressure should be the same fraction of the vapor-pressure of the substance at the same temperature. Deviations from Raoult's law have their kinetic basis in a lack of constancy of the thermodynamic environment. According to Hildebrand,[5] the most satisfactory criterion for constancy of thermodynamic environment is equality of internal pressures. The conception of internal pressure has been employed frequently for other purposes, and several methods have been devised for evaluating it for different liquids. Although the actual values yielded by the different methods differ quite considerably the relative values show satisfactory agreement.

Internal pressure is the force which, together with external pressure, counteracts the thermal pressure caused by the kinetic energy of the molecules of a liquid The tendency of molecules to escape from a solution would seem to be closely related to this property, internal pressure. For normal liquids with approximately equal internal pressures, Hildebrand finds that the observed partial pressures agree satisfac-

[1] *Jour. Am. Chem. Soc.*, Vol. **39**, p. 2126.
[2] "Die Kontinuität," van der Waals. See p 190 for van der Waals' constants.
[3] *Zeit. phys. Chem.*, Vol. **72**, p. 723 (1910).
[4] *Ibid*, Vol **36**, p 41 (1901) and Vol. **75**, p. 527 (1910)
[5] *Jour Am. Chem. Soc.*, Vol. **38**, p. 1458 (1916).

torily with those required by Raoult's law. Differences in internal pressures result in deviations from the law in the direction of greater partial pressures than the law indicates. It might be expected, naturally, that two kinds of molecules of different sizes and attractive powers would give volumes larger than those calculated on the basis of additivity. Furthermore, it might be expected that the attractions would be smaller and the tendencies to escape into the vapor-phase greater than in the case of the separate liquids. Preliminary calculations give promise that the discovery of a formal relationship between these quantities may be expected [1]

Another factor which is concerned in the deviations from Raoult's law is the polar nature of many liquids. This property has been discussed by Bray and Branch[2] and by Lewis [3] Some of the properties of typical polar substances are chemical reactivity, existence in tautomeric forms, electrical conductivity, ionizing power, high dielectric constant, and association of the molecules into complexes Typical non-polar substances have the opposite properties

As a result of polarity, there is a molecular attraction which yields a higher internal pressure than would otherwise exist. Addition compounds are formed readily, and there is a tendency for a substance to increase in polarity when it is introduced into other polar substances

A mixture of a strongly polar and a non-polar liquid generally results in the formation of a double liquid layer, and in considerable deviations from Raoult's law. Two polar liquids may show agreement with the law, but in general, one of them will be more electro-positive than the other and the vapor pressures will be smaller than the law requires.

The bearing of internal pressure and of polarity would seem to be of real moment in this field, although as yet the method is capable of indicating only the relative variations from Raoult's law The effects of the two properties upon the deviations have been summarized by Hildebrand as follows:

(1) Raoult's law should be followed by binary mixtures of non-polar liquids which have the same internal pressures, (2) non-polar liquids of unequal internal pressures yield solutions with greater vapor-pressures than required by Raoult's law; (3) a polar liquid and a non-polar liquid behave in the same way as is indicated in (2); (4) mixtures of polar liquids may show deviations in either direction, but as a rule smaller vapor-pressures than are expected, are observed

The usefulness of the above considerations in predicting the results to be obtained upon distilling a mixture of liquids, is shown by the following example [4] The results to be obtained by a fractional distillation of pairs of liquids which follow Raoult's law are predictable from the partial pressures of the constituents. Internal-pressure relationships, by indicating the nature of the deviations from Raoult's law, enable one to judge of the results in a given case in comparison with other cases which have been fully investigated. The deviations of oxygen and nitrogen have been investigated fully.[5] Since the differences in the internal pressures of oxygen and nitrogen are greater than those of nitrogen and argon, smaller deviations from Raoult's law were predicted for the latter pair of substances by Hildebrand Measurements which had been made previous to this prediction, but which were unknown to Hildebrand, are in agreement with the prediction

Partial and Total Vapor-Pressure Curves. – A system composed of a vapor and a liquid phase of a binary mixture has, according to the phase rule, two degrees

[1] HILDEBRAND, *l c*
[2] *Jour Am Chem Soc*, Vol **32**, p 1440 (1913)
[3] *Ibid*, Vol. **35**, p. 1448 and Vol. **38**, p 762 (1916)
[4] HILDEBRAND, *Jour Am Chem Soc*, Vol **41**, p 1076 (1919).
[5] INGLIS: *Proc. Phys Soc*, Vol. **20**, p. 640 (1906)

of freedom. At any given temperature, therefore, the vapor-pressure may have a continuous series of values. Obviously, these vapor-pressures are those of solutions of a continuous series of values of compositions, expressed preferably as mole fractions.

In Fig. 6, the relationships between the partial-pressure curves and the total-pressure curves for the three typical forms which have been considered, are shown.

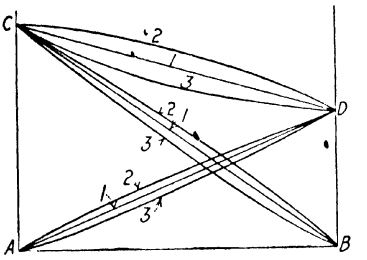


FIG. 6.

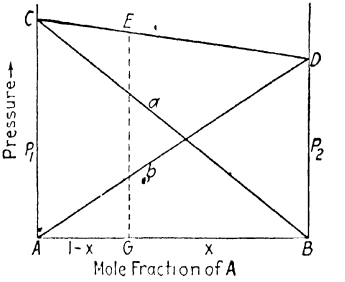


FIG. 7.

Each total-pressure curve is the sum of the partial-pressure curves of the constituents. The compositions given are those of the liquid, as has been the case for all curves so far presented.

Besides the curves which have been considered, there are several other forms which are possible. Some of these have been realized experimentally. Concerning the existence of others, there is still a division of opinion. This aspect of the subject is outside the scope of this article, and can be referred to only casually. The various possible forms of partial-pressure curves, including those with points of inflection, permit of a large variety of total-pressure curves, by their combination [1]

Form of the Vapor-Composition Curve.—It is of course true, that besides the curves showing the relationships between the compositions of the liquid mixtures and the vapor-pressures, there are curves showing the relationships between the composition of the saturated vapors and the vapor-pressures. We have already seen that the vapor-pressure curve of ideal binary solutions is of a very simple form, being expressed by the equation of a straight line. The curve which shows the relationship between the composition of the saturated vapor and the vapor-pressure is, however, not so simple even for this case.

If it is assumed that the vapors follow the gas laws, the ratios of the mole fractions of the constituents in the vapor phase are equal to the ratios of their partial pressures. Let n_1 and $1-n_1$ represent the mole fractions of A and B respectively, in the liquid phase, and n_2 and $1-n_2$ the mole fractions in the vapor phase. From Fig. 7, we see that

$$\frac{n_2}{1-n_2} = \frac{aG}{bG} = \frac{n_1 P_1}{(1-n_1)P_2} = \frac{n_1}{1-n_1}\,\frac{P_1}{P_2}$$

[1] NERNST, "Theoretical Chemistry," MacMillan, 1916, p 107, OSTWALD, "Lehrbuch der allgemeinen Chemie." 2d Ed., II, p 617 ff ; KUENEN, "Theorie der Verdampfung und Verflüssigung von Gemischen," Leipzig, 1906; MARSHALL, *Jour Chem. Soc*, Vol **89**, p 1350 (1906); KONOWALOW, *Jour. Chim. Phys.*, Vol **5**, p. 237 (1907), ZAWIDZKI, *Zeit. phys Chem*, Vol. **69**, p. 630 (1909), DOLEZALEK, *ibid.*, Vol. **64**, p. 729 (1908); BOSE, *ibid*, Vol **68**, 458 (1908), BANCROFT, "Phase Rule," Ithica, 1897, p. 116 ff.

On the other hand, since the total pressure, P, is equal to the sum of the partial pressures we have the equation

$$P = n_1 P_1 + (1 - n_1) P_2$$

From these two equations is obtained the equation of the curve for the composition of the vapor and the total pressure

$$P = \frac{P_1 P_2}{P_1(1 - n_2) + P_2 n_2}$$

This equation is that of a hyperbola. At any given pressure, the composition of the vapor is higher in the more volatile constituent than that of the liquid. For the special case that $P_1 = P_2$ (optical isomers), the curve is a single horizontal straight line for both the liquid and the vapor. It is also evident that the form of the two curves for pairs of liquids having equal values for the ratio $\frac{P_1}{P_2}$ is the same, regardless of the absolute values of these quantities. The vapor-curve lies below the liquid-curve at each composition.

As we have seen, most pairs of liquids do not yield these simple curves. The general considerations outlined above are only qualitatively applicable to most cases.

Total-Pressure Curves with Maxima and Minima. The total vapor-pressure curves for certain pairs of liquids have maximum values. In relatively fewer cases, the curves possess minima. Pairs of liquids which present these phenomena can not be separated directly by fractional distillation. It has been observed that for pairs of liquids which yield a total vapor-pressure curve with a minimum, one of the liquids is an acid and the other a substance of basic character, or that the liquids are water and certain acids. Some exceptions to these conditions are known. A list of binary mixtures which yield vapor-pressure curves with maxima or minima is given by Young [1]

In the case of these curves, the vapor composition curves lie below the liquid composition curves, both having a common tangent at the maximum or the minimum value. The vapor is not, however, uniformly richer in the more volatile component, as can be seen readily by drawing the curves.

Theory of Fractional Distillation. A quantitative basis for a theory of fractional distillation is furnished by the work of Konowalow. This theory, for the sake of simplification, is limited to binary mixtures which do not yield a vapor-pressure curve with a maximum or a minimum value. The latter mixtures may, however, be included, if the solutions are considered as binary mixtures of one or the other pure substance (the one present in excess of the composition of the mixture at the maximum or minimum), and of the solution having the maximum or the minimum vapor-pressure.

By a process which amounts to an application of the van't Hoff-Le Chatelier law of mobile equilibrium, Konowalow (*l. c.*) arrived at the following conclusion: The vapor of a binary mixture has a larger content of that constituent by the addition of which the vapor pressure of the liquid is increased, than does its equilibrium liquid.

Konowalow's course of reasoning is as follows: Upon increasing the volume of the vapor phase of a binary mixture in equilibrium with its liquid phase (constant temperature), some change must ensue which tends to counteract the change in volume. This change is a decrease in vapor-pressure. Since for the pair of liquids under

[1] "Fractional Distillation," p. 67 ff.

consideration, the curve of liquid composition and vapor-pressure slopes downward continuously from the point representing 100 per cent of the more volatile constituent to the point representing 100 per cent of the less volatile constituent, this decrease in vapor-pressure requires that the liquid have a higher percentage of the less volatile constituent than originally. By applying the above reasoning to equilibrium systems of all possible compositions, it is seen that the curve of vapor-compositions and vapor-pressures lies below the curve of liquid compositions and vapor-pressures at all points (except for the pure substances). The compositions of vapor and of liquid which are in equilibrium are represented by the points of intersection of the two curves with a horizontal line drawn through the point which shows the pressure of the system. In every case, therefore, the vapor is richer than the liquid in the more volatile constituent. A construction of the curves makes this fact very apparent.

On the basis of the results obtained by Konowalow, Golodetz[1] has outlined a theory of fractional distillation. The theory is qualitative only, but is nevertheless of some utility. If we consider A to represent the more volatile constituent and B the less volatile, the following form may be given to the statement of Golodetz's theory.

1. If a mixture of two liquids A and B is boiled, the temperature of the saturated vapor lies between the boiling points of the constituents. This temperature approximates the boiling point of one of the constituents the more nearly, the greater the concentration of this constituent in the liquid phase.

2. The vapors are always richer in the more volatile constituent than the liquid mixture.

Since the process is reversible, these principles apply in an analogous way to the fractional condensation of a saturated vapor. It should be stated that the same limitations are postulated as were stated above in the discussion of Konowalow's work.

All mathematical formulations of these principles have the same defect, they lack general applicability. After a consideration of some of the qualitative information which may be gained from these principles, we shall consider some of the quantitative treatments which have been proposed.

Measurement of Partial Pressures.—It is impossible to measure directly the partial pressures of the constituents of a binary (or other) mixture. In all of the methods employed for determining these partial pressures, the composition of the vapor in equilibrium with the solution, under the chosen conditions, is ascertained. It is then assumed that the partial pressures are proportional to the relative molecular concentrations of the constituents in the vapor. The measured total pressure and the assumed molecular weights of the constituents make possible the calculation of the partial pressures.

In most of the methods employed for determining partial pressures, a small quantity of distillate is collected from a relatively large quantity of the solution. It is the aim of the method to secure sufficient of the distillate for analysis, without changing appreciably the composition of the original solution. In the extensive investigations of Zawidzki,[2] about 1 c.c. of distillate was obtained from 100 to 120 c.c. of the solution. In some cases, certainly, the composition of the vapor does change appreciably under these conditions. Another objection to the method is the fact that water, if present in the solution, tends to pass over with the first portions of the distillate, often as the result of the formation of a solution of minimum boiling-point. Various investigators have carried out their distillations under constant pressure, while others have made them at constant temperature. An accurate method for determining partial pressures,

[1] GOLODETZ, *Chem. Ind.*, Vol. **35**, pp 102 and 141 (1912).

[2] *Zeit. phys. Chem.*, Vol. **35**, p. 129 (1900).

which is free from the above objections and which can be made to yield any desired volume of distillate having the composition of the equilibrium vapor, has been perfected by Rosanoff and Easley.[1] Rosanoff, Bacon and White[2] have devised a simple, effective laboratory method for partial vapor pressure determinations.

Boiling Point-Composition Curves.—In the case of normal liquids, the boiling-points of binary mixtures can be calculated if the vapor-pressure curves of the individual liquids are available. The molecular compositions of the mixtures having a vapor-pressure of 760 mm. at a series of temperatures between the boiling points of the pure liquids are calculated by applying the formula:

$$m = 100\frac{P_B - 760}{P_B - P_A}$$

m is the percentage molecular composition of the solution, for the less volatile constituent. P_B is the vapor-pressure of the more volatile constituent and P_A that of the less volatile constituent at the same temperature. Obviously, the same formula may be used in constructing the boiling-point curve at another pressure, by substituting the value of this pressure in place of 760 in the formula. The values of m thus obtained are plotted as abscissas against the corresponding temperatures to obtain the boiling-point curve.

The curve obtained in this manner expresses the composition of the liquid, *i.e.*, of the solution. For normal liquids, the curve is not a straight line, but rather lies below the straight line joining the boiling-points of the pure substances. The deviation from this straight line is least for pairs of liquids which have boiling-points close together.

The calculation of the composition of the vapor in equilibrium with the solution at its boiling-point, is possible for normal liquids. In accordance with the principles of Konowalow, the vapor composition curve lies above the liquid-composition curve, since the vapor contains a higher percentage of the lower-boiling constituent than its equilibrium solution. The vapor and the liquid which are in equilibrium are those which have the same temperature. In the usual diagram, therefore, in which the boiling points are plotted as ordinates, and the compositions as abscissas, any given solution is in equilibrium with that vapor which lies on the same horizontal temperature line.

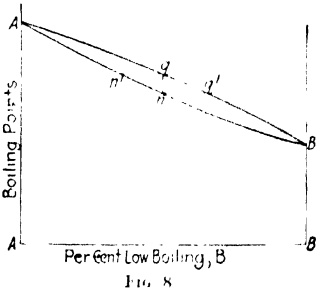


FIG. 8.

Distillation of a Binary Mixture. The behavior of a binary solution upon distillation, under such conditions that the vapor and solution remain in contact so that they are continuously in equilibrium, is shown by Fig. 8. The curve AqB is the vapor-composition curve and AnB the liquid-composition curve. The boiling-points are given as ordinates. Molecular compositions are shown as abscissas. If a solution of the composition corresponding to the point n is heated to its boiling-point, the first vapor which is formed is richer in the lower

[1] *Jour. Am. Chem. Soc.*, Vol. **31**, p. 953 (1909).
[2] *Jour. Am. Chem. Soc.*, Vol. **36**, p. 1803 (1914).

boiling constituent, B, than the original solution. Its composition may be found by reading the abscissa of q', the intersection of the vapor-composition curve, AqB, and a line drawn through n, parallel to the axis AB. The remaining solution has a lower percentage of the lower-boiling constituent and a higher boiling-point than the original solution, and is represented, therefore, by some point to the left of n on the curve AnB. Continued formation of vapor causes the composition of the solution to become progressively higher in the higher-boiling constituent, A. The points representing these compositions lie farther and farther to the left of P, on the curve AnB. When the composition of the solution reaches the value corresponding to the point n', the diagram shows that the equilibrium vapor has the same composition as the original solution. Since the total mass of vapor and liquid has remained constant throughout the distillation, it is obvious that at the point n', all of the liquid has been transformed into vapor. Just before all of the liquid has evaporated, the solution has the composition represented by a point just to the right of n'. It is obvious, therefore, that when the distillation is conducted in this manner, the maximum enrichment of the solution in the higher boiling constituent, A, is limited to a value given by the abscissa of the point n'. The proportion of the solution having this composition is, of course, very small.

The behavior of a vapor having the composition corresponding to the point q, when it is condensed gradually in the presence of the condensate formed, is shown in the same diagram. The first small portion of liquid formed is richer in the higher boiling constituent than the vapor, its composition being given by the point n'. The remaining vapor has, therefore, a higher percentage of the lower-boiling constituent, and is represented by a point to the right of q on the curve AqB. Further condensation of vapor enriches the vapor continuously in the lower-boiling constituent, the points representing the condition of the vapor lying progressively to the right of q. When the vapor reaches the condition represented by the point q', the liquid is seen to have the same composition as the original vapor. Obviously, at this point, the vapor has been completely condensed to liquid. Furthermore, it is apparent that the maximum enrichment of the vapor in the lower boiling constituent by this process is given by the point n', and also that the yield of this vapor is very small.

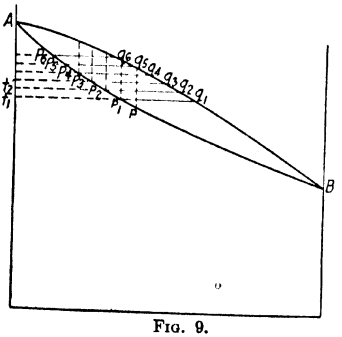


FIG. 9.

Quite a different behavior is observed if the vapor which is formed during the distillation is removed continuously or at intervals, and condensed apart. In Fig 9, the behavior upon distillation of a solution which has the composition corresponding to the point p, is shown. When the liquid has changed in composition from that represented by p to that by p_1, the equilibrium vapor is removed from the system. The remaining solution, boiling at a higher temperature, t_1, gives off further vapor, and changes in composition until the point p_2 is reached, when the vapor is again removed. By repeating this process in successive steps, the composition of the solution is seen to approach that of practically pure A, the higher-boiling constituent.

Here, too, the yield of enriched solution is relatively very small. By this process, however, it is possible to proceed to a practically pure constituent of the solution.

The fractional condensation of a binary vapor, with step-wise removal of the condensate, is shown in the same diagram. Starting with a vapor of composition corresponding to q_6, the first condensate is seen to be represented by the point p_6. After the vapor reaches the composition of the point q_5, the condensate is removed and the condensation and removal of condensate carried successively through the stages q_5,q_4,q_3, etc. The composition of the final vapor can be made, in this way, practically to reach that of the pure constituent B. The yield is again relatively very small.

By employing the preceding process of distillation, it is then possible to isolate the higher-boiling constituent in pure form. Analogously, by fractionally condensing the mixed vapors, it is possible to obtain a vapor which is the pure low-boiling constituent. Neither process alone can yield the two pure substances. Since in a given operation the yield of pure substance is negligibly small, the processes of distillation and condensation must be carried out simultaneously and repeatedly, in order to be of practical use. The elementary theoretical aspects of the operation, are, however, given in the above discussions.

Boiling-point Curves and Relative Weights of Vapor and Solution.—A valuable feature of the boiling-point-composition curves is brought out in Fig. 10. A solution of weight M and original composition P, is distilled until the solution has the composition p and the equilibrium vapor the composition q. If the weight of the solution is m, and that of the vapor n, the following relationships hold:

$M = m + n$ and $MP = mp + nq$.

From these two equations, the following is derived.

$$\frac{m}{n} = \frac{q - P}{P - p}$$

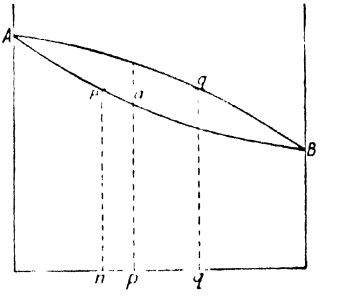


FIG. 10.

From the diagram, therefore, we see that the ratio of the weight of the solution to that of the vapor is given by the proportion $\frac{aq}{pa}$. The ratio of the weight of the vapor to that of the total is shown by pa/pq and the ratio of the weight of the liquid to the total weight by aq/pq.

Principle of Fractionating Column. The design of the usual laboratory fractionating column or of the conventional column still for commercial use is such that fractional distillation and condensation are combined and repeated a number of times. Instead of passing directly to the condenser, the vapor which leaves the flask or boiler, passes to a column with a number of compartments, separated by perforated trays or otherwise, in which partial condensation is effected by cooling. The condensate is trapped in part, so that the vapor from the boiler or from a lower compartment must bubble through the layer of condensate. In this way, an exchange of constituents between vapor and condensate is effected, so that the vapor leaving a compartment is richer in the lower boiling constituent than it was when it entered. The incoming vapor, having a temperature higher than that of the condensate in the compartment,

heats it and causes it to boil. The vapor formed from the condensate is richer in the lower-boiling constituent, as we have seen. The incoming vapor itself, which is cooled in the compartment, is partially condensed, and as we have seen, also yields a condensate which is richer in the higher-boiling constituent. The portion of this vapor which remains is therefore enriched in the lower-boiling constituent. The enriched vapor passes on to the next higher compartment and the excess of condensate flows down to the next lower compartment. The number of designs of apparatus for effecting fractional distillation both for laboratory and for plant use, is very large. The fundamental principles of nearly all, however, are those outlined above.

Changes Occurring in a Fractionating Column.—The method of operation of a fractionating column with ten trays or compartments, is shown in Fig. 11.[1] The curve AqB is the composition curve for the vapor, and Ap_1B that of the liquid. Boiling-points are plotted as ordinates. The vapor from the boiler has the composition corresponding to q, and is, therefore, already fairly rich in the lower-boiling constituent, B. Since the top tray is to deliver nearly pure B to the fractional condenser, the temperature at this part of the column must be only slightly higher than the boiling point of pure B. The temperatures on the successive trays are maintained at values such that the differences are greater for the lower pairs of trays. This provision, effected by structural features and heat-insulation, insures that the efficiency of the column shall be good, as will be shown later.

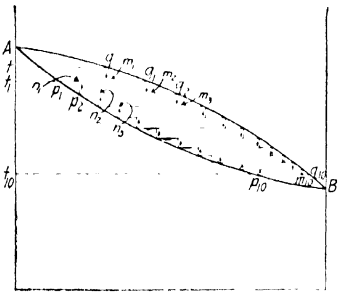


FIG. 11.—Ten-tray fractionating column.

On the first tray, the vapor, q, is fractionally condensed, its composition being changed to q_1. If the weight of vapor, q, were M, the weight of vapor q_1, is seen to be $M\frac{p_1m_1}{p_1q_1}$. This vapor then passes to the second tray, where its composition is altered to that of q_2. The weight of residual vapor is $M\frac{p_1m_1}{p_1q_1}\cdot\frac{p_2m_2}{p_2q_2}$. In the same way, we could trace the vapor through each of the trays. Obviously, the weight M', of vapor leaving the tenth tray is given by the following equation:

$$M' = M\frac{p_1m_1}{p_1q_1}\cdot\frac{p_2m_2}{p_2q_2}\cdot\quad\cdot\quad\cdot\quad\cdot\frac{p_{10}m_{10}}{p_{10}q_{10}}.$$

The factors of the right-hand member become progressively smaller, and it is obvious that much of the original vapor is returned to lower trays as condensate.

In a similar way, we could trace the course of the condensates from tray to tray. Thus, the condensate p_{10} flows to tray 9 and yields a vapor of composition q_9; and the other condensates p_9, p_8, . . . yield the vapors q_8, q_7, etc. The weights of these secondary vapors are expressed by formulas analogous to those for the primary vapor.

If the curves are drawn for the case in which the temperature intervals between each pair of trays is constant, instead of greater for the lower trays than for the upper,

[1] GURWITSCH "Wissenschaftliche Grundlagen der Erdölbearbeitung." JULIUS SPRINGER, Berlin, 1913, p. 16 ff9.

the equation for the weight of primary vapor, M'', leaving the tenth tray has the same form as that given above for M'. The first factors of the right-hand member, are smaller in the M' equation than those of the M'' equation. However, the last factors of the M' equation are relatively much greater than those of the M'' equation. The result, therefore, is that the quantity of vapor, M', is greater than M''. It is advantageous, therefore, in this case, to make the temperature differences between successive upper trays as small as possible. In the event that the vapor from the boiler is lower in the lower-boiling constituent, the efficiency of the column is increased by making the temperature differences between the lower trays small, also.

Since the requirement of small temperature differences between the trays requires a large number of trays for an ordinary separation, it is customary to take the vapor from the top tray of a column with a considerable number of trays to a fractional condenser, where the removal of the final portions of the higher-boiling constituent is effected without rectification, at this place, of the condensate (the condensate is returned to the column). This fractional condenser is in effect a constant temperature still-head, and should be maintained constantly at a temperature only slightly above that of the boiling-point of the more volatile constituent, if a pure product is desired. The vapor from the fractional condenser, which is the product of the column, is led to the cold condenser.

Importance of Number of Trays in a Column. Since the fractional condensation and distillation are effected upon the trays, it would seem to be obvious that the number of trays should be as large as possible for the sake of efficiency. The effect of decreasing the number of trays is shown in Fig. 12. If the first tray is left out, the vapor from the boiler, q, is changed on the second tray into the vapor q_2. If the weight of the vapor, q, was M, the weight of q_2 is $M \dfrac{p_2 m_2'}{p_2 q_2}$. In the event that the vapor q_1 is altered on both the first and second trays, the quantity of vapor, q_2, is $M \dfrac{p_1 m_1}{p_1 q_1} \cdot \dfrac{p_2 m_2'}{p_2 q_2}$. The latter quantity is greater than the former.[1]

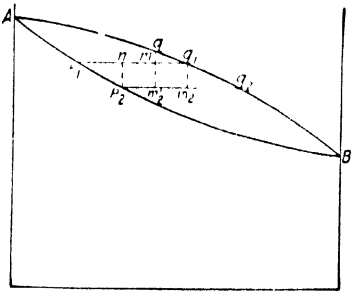


FIG. 12.—Effect of decreased trays.

Return of Condensate from Fractional Condenser. The advantage of returning all of the condensate from the fractional condenser to the top tray, rather than distributing it to several trays, is made apparent in Fig. 13. Since the vapor passing to the fractional condenser is generated from the solution on the top tray, it follows that the condensate which is formed in this condenser must be richer in the lower-boiling constituent than the liquid on the top tray

[1] If $M \dfrac{p_1 m_1}{p_1 q_1} \cdot \dfrac{p_2 m_2}{p_2 q_2} > M \dfrac{p_2 m_2'}{p_2 q_2} \cdot \dfrac{p_1 m_1}{p_1 q_1} > \dfrac{p_2 m_2'}{p_2 m_2}$.

From Fig. 12, $\dfrac{p_1 m_1}{p_1 q_1} = \dfrac{p_2 m_2' + p_1 n}{p_2 m_2 + p_1 n}$.

Since $\dfrac{p_2 m_2'}{p_2 m_2}$ is a proper fraction, the addition of the same quantity, $p_1 n$, to its numerator and denominator increases its value. Therefore, $\dfrac{p_1 m_1}{p_1 q_1} > \dfrac{p_2 m_2'}{p_2 m_2}$.

(Since it is in equilibrium with a vapor which is richer in the low-boiling constituent than the vapor which entered the condenser.) When the condensate is led off at several levels from the condenser, even the first condensate is richer in the low-boiling constituent than that on the top tray. This consideration, as well as the fact that the separation is more efficient the higher the ratio of the weight of the condensate with which the vapor is brought in contact on a tray to the weight of the vapor, shows that the condensate from the fractional condenser should pass down through all of the trays.

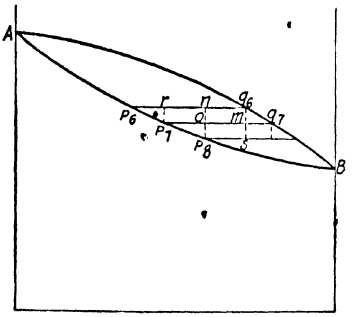


FIG. 13.—Fractional condensation.

In Fig. 13, suppose that the condensate p_8 is passed around the seventh tray to the sixth tray. It yields there vapor of composition q_6, whose weight is $p_8 \frac{p_8 n}{p_6 q_6}$. By the partial condensation of this vapor on the seventh tray, the vapor q_7 remains, and its weight is $p_8 \frac{p_8 n}{p_6 q_6} \frac{p_7 m}{p_7 q_7}$. If, however, the condensate p_8 passes first to tray seven, it is partially condensed, yielding vapor q_7 with a weight $p_8 \frac{p_7 o}{p_7 q_7}$ and condensate p_7 with a weight $p_8 \frac{oq_7}{p_7 q_7}$. The condensate p_7 then passes to tray six, where it yields vapor q_6 having a weight $p_8 \frac{oq_7}{p_7 q_7} \frac{p_6 r}{p_6 q_6}$. The vapor q_6 condenses partially on tray seven. The part which remains, vapor q_7, has a weight $p_8 \frac{oq_7}{p_7 q_7} \frac{p_6 r}{p_6 q_6} \frac{p_7 m}{p_7 q_7}$. By shunting out tray seven, the quantity of vapor q_7 obtained was found above to be $p_8 \frac{p_6 n}{p_6 q_6} \frac{p_7 m}{p_7 q_7}$, while by having both trays in operation the quantity of vapor, q_7, was $p_8 \frac{p_7 o}{p_7 q_7} + p_8 \frac{oq_7}{p_7 q_7} \frac{p_6 r}{p_6 q_6} \frac{p_7 m}{p_7 q_7}$. The latter is the larger quantity,[1] and the using of all of the trays is therefore desirable.

In the above discussion, it has been assumed that the rate of boiling of the original solution has been kept constant, *i.e.*, that the heat-consumption of the still has been maintained constant. Obviously, if a column is to effect the separation of the constituents of the solution, there must be a fall of temperature from the bottom tray to the fractional condenser, otherwise the vapor would pass the trays unchanged. In

[1] If $p \frac{p_7 o}{p_7 q_7} + p_8 \frac{oq_7}{p_7 q_7} \frac{p_6 r}{p_6 q_6} \frac{p_7 m}{p_7 q_7} > p_8 \frac{p_6 n}{p_6 q_6} \frac{p_7 m}{p_7 q_7}$

$p_7 o \cdot p_6 q_6 \cdot p_7 q_7 + oq_7 \cdot p_6 r \cdot p_7 m > p_6 n \cdot p_7 m \cdot p_7 q_7$. (By dividing out the common factor p_8, making all denominators the same and then multiplying out the denominators.)

From the figure, it is seen that the left-hand member $p_7 o \cdot p_6 q_6 \cdot p_7 q_7 + oq_7 \cdot p_6 r \cdot p_7 m = p_7 o \cdot p_7 q_7 (p_7 m + p_6 r) + oq_7 \cdot p_6 r \cdot p_7 m = p_7 o \cdot p_7 q_7 \cdot p_7 m + p_7 o \cdot p_7 q_7 \cdot p_6 r + oq_7 \cdot p_6 r \cdot p_7 m$ (Since $p_6 q_6 = p_7 m + p_6 r$).

Also the right-hand member $p_6 n \cdot p_7 m \cdot p_7 q_7 = p_7 m \cdot p_7 q_7 (p_7 o + p_6 r) = p_7 m \cdot p_7 q_7 \cdot p_7 o + p_7 m \cdot p_7 q_7 \cdot p_6 r = p_7 m \cdot p_7 q_7 \cdot p_7 o + p_7 m \cdot p_6 r (p_7 o + oq_7) = p_7 m \cdot p_7 q_7 \cdot p_7 o + p_7 m \cdot p_6 r \cdot p_7 o + p_7 m \cdot p_6 r \cdot oq_7$. (Since $p_6 n = p_7 o + p_6 r$, and $p_7 q_7 = p_7 o + oq_7$).

By comparing the expanded members, it is seen that two of the terms are alike. The second term of the left-hand member, $p_7 q_7 \cdot p_7 o \cdot p_6 r$ is greater than that of the right member, $p_7 m \cdot p_7 o \cdot p_6 r$. (Since $p_7 q_7 > p_7 m$, and the other two factors are the same in each).

practice, the proper temperature-differences between trays is maintained, for a given rate of working, by suitably insulating the column. The loss of heat by radiation, etc., beyond the quantities necessary to maintain the desired temperature-differences, is objectionable, since such loss of heat cools the liquid on a tray below its boiling-point, thereby causing a loss of heat energy, since the liquid must be reheated by the rising vapors. Cooling of the walls in contact with the vapor effects a fractional condensation and a slowing of the working of the column which can only be overcome by an increased number of trays or by an increase of the heat units supplied to the boiler.

A given column works satisfactorily only under a given rate of vapor supply, so long as its heat insulation remains unchanged. This rate must be such that the necessary fall of temperature to effect the desired fractionation can occur. If the vapor supply is decreased, the temperature falls on any given tray to such an extent that the condensation of a solution rich in the lower-boiling product is brought about, and the yield of the column is greatly decreased. If the vapor-supply is too great, the required temperature differences are not realized, and the vapor leaves the top tray with too great a content of the high-boiling material. By providing for the removal of more heat from the column, *e. g.*, by decreasing the efficiency of the heat-insulation, the desired temperature differences may be had with the increased supply of vapor. In this way the product of the same composition is obtained in increased quantity. Likewise, the ratio of the weight of the product to that of the liquid flowing back into the boiler is the same as before.

Quantitative Treatment of the Problems of Fractional Distillation.—The theory of fractional distillation of Golodetz, based upon the principles of Konowalow, is theoretically sound, but since it is purely qualitative, it can be used only in a general way in connection with problems of fractional distillation. The fundamental question to be answered by a quantitative theory of fractional distillation is as follows: What percentage of a solution of a given composition, X_0, must be removed by a simple distillation, in order to change the composition of the solution to X? The theory of Golodetz is not able to answer this question.

Earlier investigators limited their investigations to an examination of the relations between the total vapor-pressures and the vapor-pressures of the pure constituents at corresponding temperatures. The values of the partial pressures and the compositions of the equilibrium vapors were largely neglected. As a result, little progress toward a theory of fractional distillation was realized. Beginning with the work of Wanklyn[1] and of Berthelot[2] in 1863, many attempts have been made to discover a rigid mathematical relationship between the composition of the vapor and that of the solution. As has been stated before, none of these are generally applicable, although all are of some utility. The formula proposed independently by Wanklyn and Berthelot is as follows:

$$\frac{X_1}{X_2} = \frac{W_1 D_1 P_1}{W_2 D_2 P_2}$$

X_1 and X_2 are the weights of the two substances in the vapor, X_1 referring to the more volatile constituent; W_1 and W_2 the weights in the liquid; D_1 and D_2 the vapor-densities under the existing conditions; and P_1 and P_2 the vapor-pressures of the pure constituents at the temperature in question.

The extended researches of Brown[3] showed that the above formula is not generally

[1] *Proc. Roy. Soc.*, Vol. **12**, p. 534.
[2] *Compt. rend.*, Vol. **57**, p. 430.
[3] *Jour. Chem. Soc.*, Vol. **35**, p. 547 (1879); *ibid.*, Vol. **37**, p. 49 (1880); *ibid.*, Vol. **39**, p. 304 (1881).

applicable. As the result of his work, Brown proposed the formula $\frac{X_1}{X_2} = \frac{W_1 P_1}{W_2 P_2}$, which was satisfactory for a number of binary solutions. Still better agreement between observed and calculated results was found by substituting a constant, C, for the factor $\frac{P_1}{P_2}$. In general, the value of the constant, C, approximated that of the factor $\frac{P_1}{P_2}$ for normal liquids. The difference between the two quantities became greater as the divergence of the vapor-pressure curve from the simple straight-line form increased. In some cases, the substitution of $C_o + \alpha m$ for the constant, C, gave good agreement. C_o and α are constants, and m is the weight (or molecular) percentage in the liquid of the constituent which is the more volatile. Since it was observed by Brown that for some pairs of liquids the ratios $\frac{X_1}{X_2}$ and $\frac{W_1}{W_2}$ were the same whether the distillations were performed at atmospheric pressure or at considerably reduced pressure, he applied his formula successfully to the data of other investigators who made their distillations at constant pressure rather than at constant temperature. This constancy of ratios, however, is not generally true. Rosanoff and Easley[1] have made calculations on the basis of Kirchoff's equation, which indicate that for substances which do not have too great heats of dilution, the ratios are not greatly affected by quite considerable variations of temperature. (No great change in the ratio $\frac{P_1}{P_2}$ is postulated).

Brown's simple formula is probably true for pairs of liquids which have a vapor-pressure curve of the straight-line form. It is not generally true, however, as can be shown by considering solutions which have a maximum or a minimum vapor-pressure. Since these solutions have the same composition for the vapor and the liquid at the pressure of the maximum or minimum value, the constant has the value of unity.[2] This value of the constant would require that the relative compositions are the same at other pressures also, which is, of course, not the case.

Adopting Brown's equation, Barrell, Thomas and Young[3] outlined a theory of fractional distillation. The utility of this theory is quite limited.

A set of equations was proposed by Lord Rayleigh.[4] Since the partial pressures of the constituents are required for each case, and the equations are limited to dilute solutions, these formulas are not generally of use.

A rigidly accurate relationship between the partial pressures of the constituents of a binary solution and the mole fractions of the substances in the solution, is given by the Duhem-Margules equation. This relationship is based upon thermodynamic principles, the assumption being made that the mixed vapors follow the gas laws. Luther[5] and Lewis[6] have derived the equation thermodynamically. In its usual form, the equation is written as follows:

$$\frac{d \log p_1}{d \log x} = \frac{d \log p_2}{d \log (1 - x)}$$

p_1 and p_2 are the partial pressures of the constituents A and B, and x and $1 - x$ the mole fractions of A and B in the solution.

[1] *Jour. Am Chem Soc.*, Vol. **31**, p 953 (1909).

[2] $\frac{X_1}{X_2} = C\frac{W_1}{W_2}$. If $\frac{X_1}{X_2} = \frac{W_1}{W_2}$, $C = 1$.

[3] *Phil. Mag.* (5), Vol. **37**, p. 8 (1894).

[4] *Phil. Mag.* (6), Vol **4**, p. 521 (1902).

[5] OSTWALD'S "Lehrbuch," 2d Ed., Vol. **3**, p. 639.

[6] *Jour. Am. Chem. Soc*, Vol. **28**, p. 569 (1906).

A pair of solution functions for this differential equation has been proposed by Margules.[1] These functions are as follows:

$$p_1 = P_1 x^{\alpha_0} e^{\alpha_1(1-x) + \frac{\alpha_2}{2}(1-x)^2 + \frac{\alpha_3}{3}(1-x)^3 + \cdots}$$

$$p_2 = P_2(1-x)^{\beta_0} e^{\beta_1 x + \frac{\beta_2}{2} + \frac{\beta_3}{3}x^3 + \cdots}$$

p_1 and p_2, have the significance which they possess in the differential equation. P_1 and P_2 are the vapor-pressures of the pure components. $\alpha_0, \alpha_1, \alpha_2, \alpha_3 \ldots$, and $\beta_0, \beta_1, \beta_2, \beta_3 \ldots$ are constants.

The following relationships between the constants are obtained from the solution functions and the differential equation:

$$\beta_0 = \alpha_0 - \alpha_1 \qquad \beta_2 = \alpha_2 + \alpha_3 + \alpha_4 + \qquad (1)$$

$$\beta_1 = -\alpha_1 \qquad \beta_3 = -\alpha_3 - 2\alpha_4 - 3\alpha_5 \qquad (2)$$

If each of these solution functions is put into the logarithmic form, and then differentiated with reference to x, the curves of the tangents to the partial pressure curves are found to have the following form:

$$\frac{dp_1}{dx} = \frac{p_1}{x}\cdot\{\alpha_0 - \alpha_1 x - \alpha_2 x(1-x) \ldots\} \qquad (3)$$

$$\frac{dp_2}{dx} = \frac{p_2}{1-x}\cdot\{-\beta_0 + \beta_1(1-x) + \beta_2 \times (1-x) + \ldots\} \qquad (4)$$

When x has the value 1 or 0, these equations reduce to these:

$$\left(\frac{dp_1}{dx}\right)_{x=1} = (\alpha_0 - \alpha_1)P_1 \qquad (5) \qquad \text{and} \left(\frac{dp_2}{dx}\right)_{x=0} = -(\beta_0 - \beta_1)P_2 \qquad (6)$$

From Raoult's law, which is valid for dilute solutions, we have the following relations:

$$\left(\frac{dp_1}{dx}\right)_{x=1} = P_1 \qquad (7) \qquad \text{and} \left(\frac{dp_2}{dx}\right)_{x=0} = -P_2 \qquad (8)$$

Equations (1), (2), (5), (6), (7) and (8) give the following values of the constants:

$$\alpha_0 = \beta_0 = 1 \text{ and } \alpha_1 = \beta_1 = 0$$

Substituting these values in the original solution functions, the forms in which the functions are generally used are obtained:

$$p_1 = P_1 e^{\frac{\alpha_2}{2}(1-x)^2 + \frac{\alpha_3}{3}(1-x)^3 + \cdots}$$

$$p_2 = P_2(1-x)e^{\frac{\beta_2}{2}x^2 + \frac{\beta_3}{3}x^3 + \cdots}$$

In order to evaluate the constants, the experimentally determined partial pressure curve of one of the components may be used. Margules (*l c*) has devised another method which involves the determination of the tangents to the total pressure curve at the values $x = 0$ and $x = 1$.[2] Both methods of evaluating the constants are only approximate, but their accuracy is in general sufficient.

An investigation of thirteen pairs of liquids was made by Zawidzki (*l c.*), and the data were compared with the requirements of Margules solution functions. Certain of these pairs of liquids, *e.g.*, benzene and ethylene dichloride, gave the value 0 for the constants α_2, α_3, β_2, β_3, etc., and under these conditions, the functions reduce to Brown's equation. Other pairs of normal liquids gave finite values for the constants, and the agreement between the observed and the calculated values of the partial pressures were fairly good (occasional discrepancies of 4 to 5 per cent). Za-

[1] *Sitzungsber. Wiener Akad.*, Vol. **104**, p. 1243 (1895).

[2] See ZAWIDZKI, *Zeit. phys. Chem.*, Vol. **35**, p. 165.

widzki applied the formula with fair success to pairs of associated liquids by using the average molar weights of the associated substances (in the liquid or the gaseous phase) in calculating the mole fractions, x and $1 - x$.

The inadequacy of the Margules solution functions with a small number of constants, has been emphasized by Bose.[1] In the event that a large number of constants is necessary, the use of the equations is cumbersome. More satisfactory results can then be obtained by a graphical method devised by Bose[2] and Marshall.[3] Story[4] has suggested a method for using the functions by employing more convergent series than had been applied previously. His method is applicable to ternary and more complex systems, as well.

The rigidly accurate equations for the partial pressure curves have been derived by van Laar[5] by using the thermodynamic potential function and the principles given by van der Waals ("Die Continuitat"). These equations take account of the differential heats of dilution, and reduce to the simpler equations only when these heats of dilution are negligible. It is evident, therefore, that measured deviations from the simple equations (and these are the rule) are only to be expected, since the heats of dilution are not as a rule negligible. The assumption that compounds or associated forms are produced in the mixtures, is superfluous. Unfortunately, the rigidly accurate equations are not generally utilizable on account of the lack of the necessary data.

A relationship between the total and the partial pressures of certain binary mixtures has been found by Rosanoff, Bacon and Schulze.[6] The equation showing the treationship is as follows:

$$\frac{dP}{dx} = \frac{P_1 - P_2}{\log P_1 - \log P_2} \log \frac{p_1(1-x)}{p_2 x} \qquad (A)$$

P is the total pressure; P_1 and P_2 the vapor pressures of the components; p_1 and p_2 the partial pressures of the components; x and $1 - x$ the mole fractions of the components in the liquid phase. This equation holds for isothermal measurements.

The constant term, $\frac{P_1 - P_2}{\log P_1 - \log P_2}$, is calculated from the values of P_1 and P_2, obtained by expressing the experimentally determined isothermal total-pressure curve as a parabolic function in the fourth degree of x and substituting $x = 0$ and $x = 1$. The parabolic function is then differentiated, and the differential coefficient, divided by the above constant, is equated to $\log \frac{p_1(1-x)}{p_2 x}$. From this equation and the known total pressure, which is equal to $p_1 + p_2$, the partial pressures are calculated.

By an analysis of Margules' solution functions and a generalization of Raoult's law, Rosanoff and Easley[7] show how the equation derived from Equation (A) and the parabolic function can be modified to make possible the calculation of the partial pressures of binary mixtures over a range of temperatures. The combination of the two solution functions, gives the following equation:

$$\log \frac{p_1(1-x)}{p_2 x} = \log \frac{P_1}{P_2} + \alpha_2\left[(1-x) + \frac{1}{2}\right] - \frac{\alpha_3}{2}\left[(1-x)^2 - \frac{1}{3}\right] + \frac{\alpha_4}{3}\left[(1-x)^3 - \frac{1}{4}\right]$$

[1] *Zeit. phys. Chem.*, Vol **71**, p 637.
[2] *Physik. Zeit.*, Vol **8**, p. 353 (1907).
[3] *Jour. Chem. Soc.*, Vol. **89**, p 1350 (1906).
[4] *Zeit. phys. Chem.*, Vol. **71**, p 129.
[5] *Zeit. phys. Chem.*, Vol. **72**, p. 723–9.
[6] *Jour. Am Chem. Soc.*, Vol. **36**, p. 1993 (1914).
[7] *Jour. Am Chem. Soc.*, Vol. **31**, p 953 (1909).

In all cases where the heat of dilution is small, the constants α_2, α_3 and α_4 are independent of the temperature over a considerable range. Changes of temperature influence the composition of the vapor only through the term "log $\frac{P_1}{P_2}$." It is only necessary, therefore, to express this ratio as a function of the temperature for the desired range. The equation for isothermal values derived as described above, has the following form:—

$$\log \frac{p_1 (1 - x)}{p_2 x} = b + cx + dx^2 + ex^3$$

If any such expression for a temperature within the range is worked out, it may be converted as follows into an equation which holds throughout the range. From the right-hand member, subtract the logarithm of the ratio, $\frac{P_1}{P_2}$, for that temperature, and add the logarithm of the function which shows how the ratio depends on the temperature.

By employing this relationship, Rosanoff, Bacon and Schulze[1] have devised a theory of fractional distillation. For organic liquids, which have small heats of dilution (α_2, α_3, α_4, etc., independent of temperature over a considerable range), the necessary data are limited to the isothermal total pressures of the solutions at a temperature not too different from the temperatures existing during the distillation and the form of the function showing the relation between the ratio P_1/P_2 and the temperature.

The derivation of the equations for showing the course of a distillation without reflux condensation is carried out as follows. If w_1 and w_2 are the weights of the constituents in the liquid, and dw_1 and dw_2 the weights in the vapor, the following relationship holds.

$$\frac{p_1 (1 - x)}{p_2 x} = \frac{w_2 \, dw_1}{w_1 \, dw_2}$$

or

$$\frac{d \log w_1}{d \log w_2} = \frac{p_1 (1 - x)}{p x_2} \tag{1}$$

From equation (A), showing the relationship between the total and partial vapor-pressures (supra),

$$\log \frac{p_1 (1 - x)}{p_2 x} = k \frac{dP}{dx} \tag{2}$$

where k is the reciprocal of

$$\frac{P_1 - P_2}{log\, P_1 - log\, P_2}.$$

This equation may be written

$$\frac{p_1 (1 - x)}{p_2 x} = e^{k \frac{dP}{dx}} \tag{3}$$

From (3) and (1) we obtain

$$\frac{d \log w_1}{d \log w_2} = e^{x \frac{dP}{dx}} \tag{4}$$

If the molar weights of the constituents are M_1 and M_2,

$$\frac{x}{1 - x} = \frac{w_1/M_1}{w_2/M_2}, \text{ which yields}$$

$$d \log (w_1/w_2) = \frac{dx}{x (1 - x)} \text{ or}$$

$$d \log w_2 = d \ln w_1 - \frac{dx}{x (1 - x)}. \tag{5}$$

[1] *Jour. Am. Chem Soc*, Vol **36**, p. 1993 (1914)

From (4) and (5)

$$d \log w_1 = \frac{e^{k \frac{dP}{dx}} dx}{(e^{k \frac{dP}{dx}} - 1)(1 - x)x} \qquad (6)$$

If the initial weight and the initial mole fraction of the first component are w_1' and X_o, respectively,

$$\log \frac{w_1}{w_1'} = \int_0^x \frac{e^{k \frac{dP}{dx}} dx}{(e^{k \frac{dP}{dx}} - 1)(1 - x)x} \qquad (7)$$

For the second component, the solution is

$$\log \frac{w_2}{w_2'} = \int_{(1-x_0)}^{(1-x)} \frac{dx}{(e^{k \frac{dP}{dx}} - 1)(1 - x)x} \qquad (8)$$

where w_2' and $1 - x_0$ are the initial weight and mole fraction of the second constituent.

The integration indicated may be performed by any of the methods of approximation. Since $w_2 = \frac{1 - x}{x} \frac{M_2}{M_1} w_1$, only one of the integrations needs to be performed.

If the total and partial-pressure curves are straight lines, equation (4) reduces to Brown's equation, and the integrals assume a simpler form.

Obviously, the theory is applicable to all cases in which the relationship (equation *A*, p. 634,) between the total vapor-pressure and the partial vapor-pressures is valid.

Constant Temperature Still-heads.—Enrichment of a binary vapor in the lower-boiling constituent may be effected by fractional condensation in a single constant-temperature still-head or in a series of such still-heads. Warren used such an apparatus for the fractionation of such complex mixtures as crude petroleum, coal-tar, etc., in 1864. In the use of this still-head, the principle of cooling is depended upon, as the washing of the vapor with the condensate is quite incomplete.

The use of a constant-temperature still-head for separating binary mixtures, was investigated by Brown.[1] For the pairs of liquids used, Brown found a very simple rule to hold: Whatever the composition of the liquid in the boiler, the vapor leaving the still-head had a constant composition, depending only upon the temperature of the still-head. This composition was the same as that of the vapor which was in equilibrium with the particular binary mixture which boiled at the temperature of the still-head (at the pressure of the distillation). By maintaining the temperature of the still-head only slightly higher than the boiling-point of the lower-boiling constituent, Brown was able to affect the separation of quite pure products.

Young and Thomas[2] have secured very good results in fractionating the low-boiling fractions of Pennsylvania crude oil by using a constant-temperature still-head above a Young and Thomas dephlegmator. The fractional condenser above certain of the column stills is an example of this practice.

Rosanoff and Bacon[3] have found that for binary mixtures which have maximum or minimum boiling-point curves, Brown's rule must be modified. The composition of the constant-boiling mixture is, of course, not altered by the still-head. In using the

[1] *Jour. Chem. Soc.* Vol **39**, p. 517 (1881).
[2] *Jour. Chem. Soc.*, Vol. **71**, p. 440 (1897).
[3] *Jour. Am. Chem. Soc*, Vol. **37**, p. 301 (1915).

boiling-point curves for ascertaining the effect of a constant-temperature still-head, the usual diagram must be divided into two portions by passing an axis of ordinates through the composition representing the mixture of maximum or minimum boiling-point. The portion of the diagram to each side of this axis must be treated as a binary mixture, the constituents being the constant-boiling mixture on the one hand, and one of the pure constituents, on the other. As can be seen readily by drawing the curves for liquids having a minimum-boiling mixture, each temperature between the boiling-point of the lower-boiling constituent and that of the constant-boiling mixture is the boiling-point of two solutions of quite different compositions. The vapors emitted by these two solutions at the boiling-point are likewise quite different. Rosanoff and Bacon find that the composition of the vapor leaving the constant-temperature still-head is constant for the cases being considered also, but that it depends upon the concentration of the solution charged into the boiler in this way. If the composition is represented in that part of the diagram to the right of the axis drawn through the point representing the solution of constant boiling-point, the vapor will have the composition corresponding to that solution having the boiling-point equal to the still-head temperature, as shown in this portion of the diagram. If the composition of the original solution is found in the portion of the diagram to the left of the axis, the composition of the vapor leaving the still-head is located in this portion of the diagram.

The behavior of the ternary system carbon tetrachloride, toluene and ethylene bromide, when distilled through a constant temperature still-head, has been studied by Rosanoff, Schulze and Dunphy.[1] Solutions of these substances yield boiling-point curves and a boiling-point surface free from maxima and minima. The authors state their conclusions as follows:

"In distillations with a still-head maintained at a constant temperature, the composition of the distillate is at every instant identical with that of a vapor evolved by a mixture whose boiling-point equals the temperature of the still-head. If the mixture is binary, the composition of the distillate is, in the course of a single distillation, constant. In those cases in which the binary boiling-point curve passes through a maximum or a minimum, the composition of the distillate depends on that of the mixture originally placed in the still. If the number of substances in the mixture is three or more, the composition of the distillate not only depends on that of the original mixture, but varies in the course of a single distillation. This variation, however, is moderate, and the nearer the constant temperature of the still-head is to the boiling-point of the most volatile component, the more nearly constant is the composition of the distillate."

The conclusions embodied in the last sentence are based upon the results with the one ternary system, and are probably too broad for some cases. Regulated temperature still-heads are nevertheless interesting in their action, and offer a promising field of investigation in connection with their commercial application.

Quantitative Treatment of Fractional-distillation Problems.—In Hausbrand's[2] "Operation of Rectifying and Distilling Equipment" complete sets of equations are presented for solving the problems of fractional distillation as carried out in commercial equipment. Although a number of simplifying assumptions are made, the results obtained with the various mixtures dealt with (binary) are sufficiently accurate for purposes of operating or designing commercial equipment. Both the heat economy and the degree of separation of the constituents obtained are considered by Hausbrand. In order to use these equations, it is necessary that the liquid composition-boiling-point curve, the vapor composition-boiling-point curve, and the heats of evaporation of the constituents be accessible.

A discussion of these equations can not be undertaken here. They are, however,

[1] *Jour. Am. Chem. Soc.*, Vol **37**, p 1072 (1915)

[2] "Rektifizier-und Destillier-Apparate," E. HAUSBRAND, 3d ed., Julius Springer, Berlin, 1916.

approximate formulas, based upon the principles outlined above. Quantitative treatment of some of the problems of fractionation are also given by Lewis[1] and by Gay.[2] The basis of treatment is in both cases similar to that of Hausbrand.

Solutions containing more than two constituents may often be treated as binary mixtures, by choosing the most volatile constituent and the sum total of the others as the components.

Sublimation.—Solid substances possess definite vapor-pressures at given temperatures, just as is the case with liquids. The process of vaporizing a solid is called sublimation. The process may be carried out on a solid below its melting point at the pressure employed, by continuously supplying heat. The number of heat units required per gram of substance is the heat of sublimation, which is analogous to the heat of evaporation of a liquid. The quantity of heat liberated when a gram of vapor condenses is numerically equal to the heat of sublimation of the same substance at any given temperature. Sublimation curves are in all respects analogous to vapor-pressure curves. The molar heat of sublimation, which is the number of heat units required to volatilize one gram mole of a solid, is strictly analogous to the molar heat of evaporation, and problems of sublimation are dealt with by methods which parallel those of distillation.

The melting-points of certain substances are higher than the temperatures at which the vapor-pressures reach the value of one atmosphere. When heated at pressures below this value, therefore, it is impossible to melt these substances. All of the heat furnished is used up in heating the solid to its "boiling-point," i.e., the temperature at which the vapor-pressure equals the external pressure, and in subliming the solid. By increasing the external pressure sufficiently, it is possible to raise the "boiling-point" of such solids above the melting points at the pressures used. By this expedient, it is possible to liquefy these substances.

In subliming mixed solids which do not form solid solutions, the relationships are the same as those discussed above for immiscible liquids. In general, the processes which are carried out practically, aim to separate one substance from others which may be considered non-volatile under the conditions used. For example, crude sulphur is sublimed in order to recover practically pure sulphur. The non-volatile earthy residue is then discarded.

The sublimation of solid solutions has not received much consideration. From the theoretical side, the treatment of the problems involved is in practically all ways the same as that of the problems of miscible liquids. Experimentally and practically there is the difference between the two cases, that in reestablishing equilibrium the exchange of constituents between the vapor phase and the other phase is not so readily effected with solid solutions as with liquid solutions.

DESTRUCTIVE DISTILLATION

By D. Drogin[3]

The process of destructive or dry distillation, also known as cracking as in the case of petroleum, consists primarily of heating organic substances such as coal, wood, shale, petroleum, tar, asphalt, etc., in a still, furnace or retort, in the

[1] *Journ. Ind. and Eng. Chem.*, Vol. 1, p. 522 (1909).

[2] *Chimie et Industrie*, Vol. 3, p. 157 (1920).

[3] Petroleum engineer, 961 Frelinghuysen Ave., Newark, N. J.

absence of air or in the presence of a limited supply, with the object of making from these substances products of industrial value, as well as to obtain residues of commercial importance. The yield of the products obtained, their quantity and quality, depend largely on several factors, the important ones being: (*a*) the kind of still, furnace or retort used; (*b*) the volume, and in case of a solid, the size of the particles constituting the charge; (*c*) the degree of heat employed in the distillation; (*d*) the use of reduced, atmospheric or increased pressure; (*e*) whether or not steam is used; (*f*) the presence of a catalytic agent, and finally; (*g*) on the manner of condensation and purification of the ensuing vapors.

The chemical changes involved in the process of destructive distillation are based on the fact that the subjecting of hydrocarbons, whether solid, liquid or gaseous to a high temperature tends to break down the more complex molecules into simpler molecules. Thus, in the destructive distillation of coal, the following reactions take place: Solid coal→*high molecular weight paraffins*→*low molecular weight paraffins*→ acetylenes, naphthenes and polycyclic compounds→benzene and its homologues.[1]

Oil Cracking.—The main products of cracking paraffin oils at low temperature (400–500°C.) are paraffins and olefines. At about 700–800°C. aromatic bodies like benzene, or toluene, are formed, together with olefines, diolefines and small quantities of paraffins. The more complicated the molecule the more readily it decomposes. This also holds true for unsaturated hydrocarbons. At the highest temperature there is complete decomposition of hydrocarbons into their elements. These changes are much influenced by alteration in temperature, pressure and catalysis.

In general, it may be said that the paraffins begin to break up at much lower temperatures than the aromatic compounds and that their decomposition is progressive, *i.e.*, the high molecular weight paraffins go to low molecular weight paraffins and higher olefines. The olefines then break up into carbon, methane, acetylene and hydrogen. The paraffins again break to olefines and paraffins and the methane finally breaks down in carbon and hydrogen.

Recent investigations by Rittman[2] and others as to the thermal reactions of petroleum and coal tar hydrocarbons show that the series of products formed by the cracking reaction under considerable pressure are as follows.

Heavy hydrocarbons⇄light hydrocarbons, saturated and unsaturated⇄cymene⇄ xylene ⇄ toluene ⇄ benzene, naphthalene, diphenyl, etc.⇄anthracene⇄carbon and gas. Although reversible the reactions take place almost entirely in the forward →direction.

Egloff and Twomey[3] showed that at atmospheric pressure the order of the reaction is the same, namely, higher benzene homologues→benzene (diphenyl)→naphthalene →anthracene→carbon and gas.

An increase of temperature favors the production of substances whose formation is accompanied by the absorption of heat *i.e.*, endothermic bodies; conversely, the formation of bodies whose formation is attended by the evolution of heat, *i.e.*, exothermic bodies, is checked by rise of temperature.

The use of steam in the process of destructive distillation is to aid the production of hydrocarbons at as low a temperature as possible. Ordinarily, these hydrocarbons would come over at their boiling point at atmospheric pressure.

[1] M. C. Whitaker and W. R Crowell, *Jour Ind Eng Chem*, Vol **9**, 1917, pp 261–269.
[2] W. F Rittman, C B Dutton and E W Dean, *Journ Ind Eng Chem*, Vol **8**, 1916, pp. 351–361.
[3] G. Egloff and T. J. Twomey, *Journ Phys Chem*, Vol. **20**, 1916, pp 121–150.

But, with the introduction of steam, the vapor pressure of the mixture, being the sum of the partial pressures of the hydrocarbon vapor at that temperature and the water vapor, is equal to the atmospheric pressure. Therefore, the hydrocarbons come over at a temperature below their boiling points. Either superheated or wet steam is used.

The use of steam is recommended in the destructive distillation of shale in Scotland. The steam equalizes the temperature in the retorts, preventing excessive cracking of the oil vapors and reducing the amount of unsaturated hydrocarbons. It increases the yield of ammonia and prevents the formation of nitrogen compounds of an undesirable nature, such as pyridine. According to C. W. Botkin,[1] steam distillation increases the yield of oil a few gallons per ton and the specific gravity of the oil thus obtained is higher by 0.03 to 0.04 than when a dry distillation is made. The yield of NH_3 is increased two to three-fold when steam distillation is used.

Winchester,[2] in six tests to determine the comparative values of steam and dry distillation in the yield of oil from shale in Colorado and adjacent areas, found that with four out of the six samples from the same lot of shale the use of steam causes an increased yield of from 10-50 per cent of that obtained with dry distillation.

There are certain disadvantages in using steam in connection with shale distillation. It increases the volume of volatile products formed. This requires the use of a large condensing apparatus. The oil and water when condensed, form an emulsion which is very slow in separating by settling. The heat units carried away from retort by steam nearly equal what are required to decompose the shale.

In the destructive distillation of resinous wood, steam is introduced to extract the turpentine already present in the wood. Steam also takes part in the production of important gaseous fuels, such as water gas, which is formed by drawing air with steam through a deep bed of coke in a closed retort. The reactions which take place are three in number:

$$C + 2H_2O = CO_2 + 2H_2$$
$$C + H_2O = CO + H_2$$
$$CO + H_2O = CO_2 + H_2$$

The course of the reaction between the steam and carbon depends chiefly upon the temperature. At 600°C. (1,112°F.) the products are principally $CO_2 + H_2$; at higher temperatures less CO_2 is formed and more CO; at 1000°C. (1,832°F.) the reaction is nearly that represented by the equation: $C + H_2O = H_2 + CO$.

The effect of pressure on petroleum cracking can be said to be as follows: Increase of pressure favors the formation of products occupying a smaller volume, conversely a diminution of pressure favors the production of substances occupying an increased volume. Generally, an increase of pressure favors the formation of unsaturated compounds and carbon.

Destructive distillation under pressure provides a considerable output of "cracked" gasoline in the United States.

In the vacuum process of distillation a partial vacuum is created in the still by the aid of a pump. The stills employed are generally of the same type as the ordinary horizontal crude still, but smaller, heavier and strongly braced. The hydrocarbons come over at a temperature considerably lower than their boiling points at atmospheric pressure. There is an improvement both in the quantity and quality of the distillation products when vacuum distillation is combined with steam distillation.

[1] C. W. Botkin, *Quarterly*, Colo. School Mines, 4, No. 4, 16–17 (1919).
[2] D. E Winchester, U. S. G. S., *Bull.* 641-F, 139–98 (1916).

Catalysis.—Chemical changes can be made to take place more readily in the presence of a catalyst. The temperature need not then be so high and the reaction can be conducted with a greater degree of ease and a smaller loss. The vapors generated in the destructive distillation of heavy oils and petroleum residues are caused to come in contact with catalytic materials heated to a high temperature ranging from 400°C. up. These materials may consist of finely divided metals, which are prepared by reducing the corresponding oxides with a reducing gas at an elevated temperature;[1] or heated graphite, aluminum chloride, iron shavings, fullers earth, metallic oxides and coke. Some catalysts are readily poisoned by the sulphur in the oils.

T. T. Gray[2] has developed a very interesting process for the decolorization and purification of the distillates obtained from cracking processes as well as those obtained by the distillation of crude petroleum by the usual methods, in which the products to be purified are passed in contact with fullers earth, bauxite, nickelized fullers earth or other catalysts maintained at a temperature sufficiently high to keep the products treated in vapor form. By this method undesirable compounds are recomposed or polymerized and removed by the catalyst. It is probable that hydrogenation takes place when the vapors containing cracked hydrocarbons and hydrogen come in contact with the catalyst. By this process it is possible to make products of merchantable color without treatment with sulphuric acid and it is said to increase the yield of gasoline obtained by pressure or other such treatment from 12 to 14 per cent. It can be applied to any cracking process or still operation and it is thought it will eliminate the acid treatment of all these products.

Destructive Distillation of Shale.—If a shale is subjected to destructive distillation the products of value obtained from it are oil, ammonia and inflammable gas. All shales do not give similar results. Those from Scotland furnish more ammonia and less oil than shales from the United States. The form of retort in which the shale is distilled and the conditions under which the distillation is conducted are largely responsible for the yields obtained.

The distillation of shale is at present an important industry in Scotland. In forty-five years, from 1871–1916, the production of shale oil rose from 593,310 bbl. to 1,965,000 bbl. and that of ammonium sulphate from 2,350 tons to 59,400 tons. The average yield of the main products obtained from a short ton of shale retorted is as follows: Crude oil, 24.5 U. S. gal.; ammonium sulphate, 35.7 lb.; gas, 9,800 cu. ft. (240 B.t.u. per cubic foot); spent shale, 80–85 per cent.

In America the industry has not as yet gained a foothold, though an unusually large number of processes exist for the retorting of the shale. In this country the shales differ widely in physical and chemical properties. It is, therefore, not commercially feasible to adopt a single type of retort for all.

The oil in shale usually does not exist in the free state, but is produced in the process of destructive distillation from an oil-forming substance known as "kerogen." The oil is highly unsaturated and is composed largely of hydrocarbons of the paraffin, olefin and diolefin series, a small amount of naphthenes, benzenes and 1 per cent of nitrogen.

For retorting shale in Scotland the Pumpherston type of retort used in the Pumpherston works, gives the best results. Several advantages are combined in it, for it is simple and economical in construction. The feed is continuous, likewise the removal of the oil, gas and spent shale.

[1] Sabatier and Mailhe, U. S. Pat. 1124333 (1915).
[2] T. T. Gray, U. S. Patent 1340889 (1920).

The retort is circular throughout, vertical and tapers. The upper part is made of cast iron about 12 ft. high, 2 ft. in diameter at the top and 3 ft. at the bottom. The lower part is made of firebrick and is about 18 ft. high and about 3 ft. in diameter at the top where it joins the iron portion. The average capacity per day is four and a half short tons per retort.

The retort is heated by the permanent gases resulting from the destructive distillation of the shale. This is supplemented by producer gas when there is a shortage of permanent gas.

During the process of distillation, steam is introduced. About 750 to 1,000 lbs. of steam are used for every ton (2,240 lbs.) of shale retorted. The advantages of steam are manifold. The temperature in the retort is rendered uniform by the transfer of heat from the walls of the retort to the center of the charge. It minimizes the cracking of the oil; it helps to sweep the oil vapors out of the retort; it cools the spent shale and it aids in the production of ammonia and water gas.

The steam is decomposed when it comes in contact with the red hot shale. The hydrogen unites with the nitrogen in the shale to form ammonia, and the oxygen combines with the carbon to form water gas.

The distillation of shale is carried out in the following way. Pieces not larger than 6 in. square are delivered to a hopper at the top of the retort and fed to the retort by gravity. The upper part is heated externally to a dull red heat. The temperature at this point ranges from 600–700°F.

In the lower part of the retort the temperature of the shale is about 1,700–1,800°F. In this part most of the ammonia and water gas is formed by the action of the steam. The spent shale is discharged from the retort into a sealed hopper, into which steam is admitted.

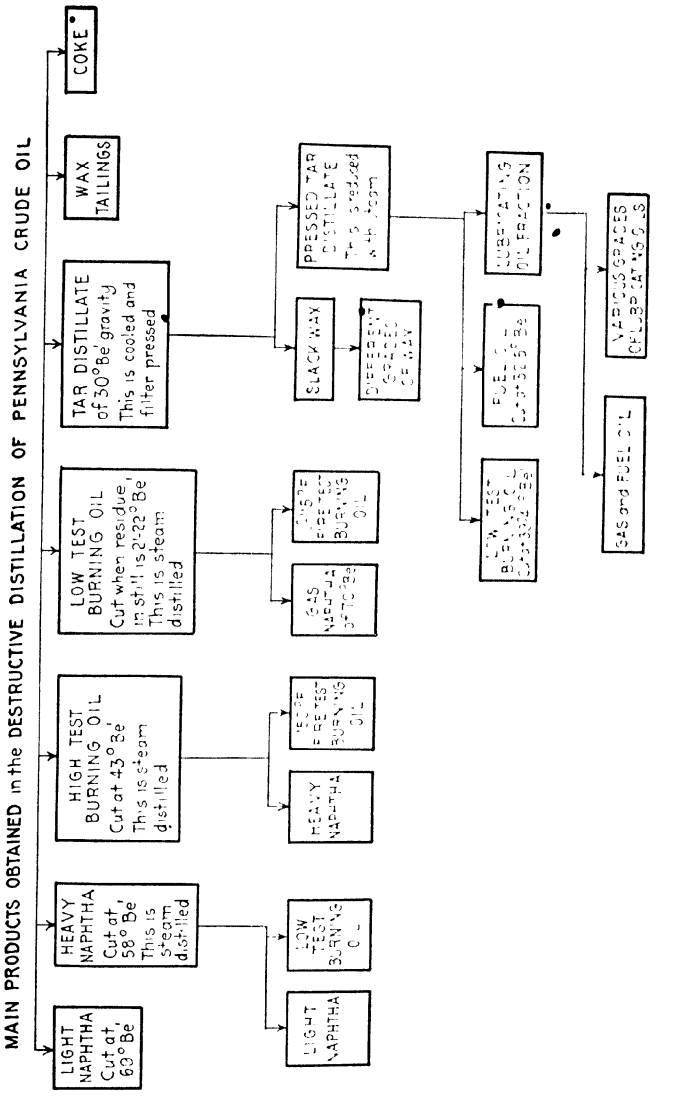
The oil and water vapors and the gases consisting of ammonia, hydrogen, carbon monoxide, carbon dioxide and some free nitrogen, enter a common main about 30 in. in diameter. The main leads the gases and vapors into a water heater, where water for the steam boiler is heated in pipes, then through air-cooled vertical condensers. The condensed oil and water vapors are led into separators where the ammonia water is separated from the oil. The gases are passed into a water scrubber to remove last traces of ammonia and then into a naphtha scrubber where the gas is washed with mineral oil to absorb the naphtha. The gases are then used as fuel for heating the retort.

The ammonia water obtained from the separators and scrubbers is distilled, and the ammonia is passed into sulphuric acid to form ammonium sulphate.

The crude shale oil as well as the scrubber oils, are fractionally distilled. Scotch shale oils suffer an average refining loss of 25 per cent. There is only about 7 per cent loss in completely refining petroleum.

The percentage yield and the products obtained from the shale oil largely depend on the nature of the shale treated and on the conditions of retorting and refining. The products obtained from shale oil in a large plant in Scotland are as follows:

	Per Cent
Naphtha (including scrubber naphtha)	9 9
Burning oil	21 7
Gas and fuel oil	24 4
Lubricating oil	6 6
Wax	9 5
Still coke	2 0
Loss	22.9
	100 0



Destructive distillation of petroleum is employed when a large yield of gasoline and illuminating oil is desired. This form of distillation is especially adapted to crudes containing little gasoline or kerosene (California and Mexican) or those unfit for the manufacture of cylinder stock (Mexican).

Horizontal underfired cylindrical stills having charging capacity of from 200 to 1,200 bbls. are generally used in the distillation of crude oil. A still with charging capacity of 500 bbls. is 10 ft. in diameter and 40 ft. long. A 1,000-bbl. crude still is 14 ft. 6 in. in diameter and 40 ft. long. In cracking processes the upper part of the still is generally left exposed to the air. In the ordinary process of distillation the stills are completely bricked in, so that the vapors shall be kept fully heated until they escape to the vapor pipe. The continuous operation in petroleum distillation does not permit of sufficient cracking to obtain highest yields of light products.

In case of a crude of paraffin base the distillation is usually carried out in a tower still. This is an ordinary still provided with an aerial condenser through which the vapors must pass before entering the water-cooled condenser. The oil is fire stilled and the heavy vapors which condense in the top of the still and in the aerial condenser fall back in the superheated oil and are thereby cracked or partially decomposed. The distillation is carried down without interruption to coke, thus separating the products as naphtha, illuminating oils and paraffin oils in one distillation.

In the accompanying charts are indicated the main products obtained in the destructive distillation of a paraffin base crude (Pennsylvania) and a mixed crude (Mid-continent).

When a large yield of lubricating oil of good quality is desired from crude petroleum, the distillation is begun in the ordinary way. Steam is let into the oil when the temperature in the still is about 230°F. and the crude naphtha is distilled off when the still temperature is about 280°F. Without steam the temperature would be about 375°F. Likewise the heavy crude naphtha is over with steam at a still temperature of about 330°F. Without steam the temperature would be about 475°F. The lamp oil is over at the still temperature of 500°F. compared with 630°F. when no steam is used. The amount of steam is gradually increased and the distillation is conducted as rapidly as possible in order to avoid cracking until the wax distillate has distilled over. The still temperature is now 620°F. The residue consists of cylinder oil stock.

Steam is always used when cracking is to be avoided. It passes up through the oil as a gas and is condensed with the oil vapors. The maximum temperature attained with steam in oil distillation is about 600°F. Without its use the still would have to be heated to a temperature of about 750°F. Such temperature would result in obtaining an oil below the desired standard. The use of steam, therefore, avoids destructive distillation.

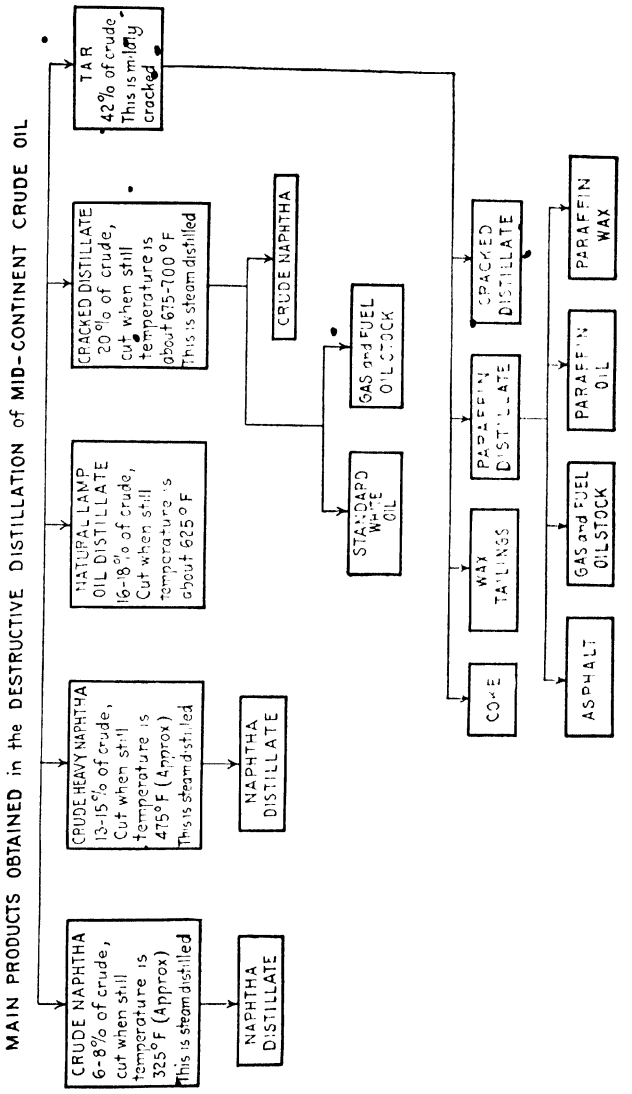
When distillations are carried on at increased pressures the charge usually consists of heavy oils or petroleum residues like fuel oil and gas oil. The stills employed when high pressure and temperature is used are of various shapes and construction. They may consist of the following: (1) heavily constructed retorts; (2) vertical stills; (3) cracking tubes; (4) combination of stills and cracking tubes; (5) horizontal cylindrical reservoir in series with multiple connected heating tubes; (6) column stills in combination with an horizontal still; (7) still internally divided in compartments; (8) shell stills; (9) rotating stills.

The technical processes for making motor gasoline and motor fuel by destructive distillation products at high pressure and temperature, employ either stills, tubes, or special catalytic methods.

R. F. Bacon and C. W. Clark[1] have found that the yield and quality of gasoline begins to decrease at pressures below 100 lb. in the still and that about 300 lb. is the upper limit for practical purposes. The percentage of saturated hydrocarbons is greater when the distillation is carried out at pressures about 100 lb. than at pressures below it.

In the Burton process stills having a capacity of about 250 bbl. are used. Petroleum residues are distilled at a temperature of 370–420°C. at a pressure of about 80

[1] R. F. Bacon and C. W. Clark, U. S. Pat. 1101482.



lb. per square inch. This pressure is maintained by means of a valve placed at the outlet of the condenser. Heavy coke forming fractions settle out at the bottom of the stills when high boiling hydrocarbons are cracked and if not removed lead to local over heating of the still bottoms with all the attendant inconveniences arising therefrom during the course of distillation. To overcome these difficulties many schemes

have been patented employing in general such methods as water-cooled jackets, circulation of the oil from one still to another one through a trap in which the coke forming substances are deposited; the use of scrapers, etc.

The Hall process embodies the use of tubes. The oil is vaporized and passed through a system of continuous coils each about 600 ft. long and 1 in. in internal diameter. It is fed in with a pressure of 50–75 lbs. per square inch at the rate of over 70 gal. per hour. It enters at the cooler end of the retort and is gradually heated and vaporized. These vapors attain a speed of 500–6,000 ft. per second in the last portion of the coil where the temperature is the highest. It is claimed that any material deposit of carbon is prevented by incomplete cracking and the high rate of flow. When working for gasoline the temperature of the exit tube is kept at 500–600°C.

The Valpy Lucas and the McAfee processes both make use of special catalysts. In the former[1] a mixture of oil and steam is brought in contact with a heated catalyst such as nickel or other metal or metallic oxide. The oil to be cracked is vaporized by super-heated steam in a separate still and the vapors are run through a cracking tube packed with the catalyst and heated to 550–600°C.

In the McAfee process[2] the crude is first heated to free it from water. Anhydrous aluminum chloride is added and the mixture boiled between 500–550°F. for 24–48 hr. Between the still and final condenser are placed two aerial condensers connected in series which separate the low boiling oils from the high boiling fractions returning the latter to the still together with any volatilized aluminum chloride. The distillate obtained contains a mixture of gasoline, solvent oil and kerosene. The products are claimed to be all water-white, sweet smelling and saturated. Later[3] McAfee combined the aluminum chloride process with the action of an ordinary pressure still in such a way that the yield of light naphtha from the latter is materially increased.

Rittman and Egloff show that starting with an oil consisting almost entirely of paraffin hydrocarbons, it is possible to produce by cracking various aromatic hydrocarbons. The method pursued is as follows: High molecular weight paraffins when subjected to destructive distillation after being first converted to paraffins of lower molecular weight and olefines, are further converted into acetylenes, naphthalenes and polycyclic compounds. The final products are benzene and higher and lower homologues of benzene.

Destructive Distillation of Asphalt.—Asphalt is a black non-oxidized bituminous hydrocarbon occurring in the heavy residuum from petroleum or in natural deposits. The residues from petroleum are known as oil asphalts and come largely from California, Mexican, Texas and Mid-continent petroleums. The most commonly used natural asphalts are Trinidad, Bermudez, Cuban and Gilsonite.

Asphalts on destructive distillation first melt; at about 300°C. vapors arise, which when condensed yield a colorless liquid with concentrated petroleum odor; at about 300°C. decomposition begins, H_2S is evolved and odor of the distillate changes. The residue consists of porous coke.

Asphalt hydrocarbons begin to decompose at a temperature of 600°F. or slightly below it. The destructive distillation yields distillates which are highly unsaturated. The proportion of unsaturated hydrocarbons in distillates from asphalts and pyro-asphalts is generally much greater than is to be found in crude-oil distillates, particularly of the paraffin and semi-paraffin type.

The destructive distillation of Gilsonite[4] yields 25–30 per cent coke, 10 per cent

[1] English patent, 20170 (1913)

[2] A. M. McAfee, *Trans. Amer. Inst Chem Eng* 1915, Vol. **8**, pp 177–95.

[3] U. S. Patent 1326073 (1919).

[4] C. F. Mabery, *Jour Amer. Chem. Soc*, Vol **39**, 1917, pp. 2015–2027.

gas, largely methane; and 60–65 per cent liquid distillate which is highly unsaturated. It contains hydrocarbons of the series C_nH_{2n-2} and a considerable amount of ammonia. Assyrian asphalt[1] containing no sulphur on destructive distillation gave 4 8 per cent water; 45.9 per cent liquid distillate resembling that of petroleum; 43 5 per cent coke and 6.3 per cent gas and loss.

The destructive distillation of asphalt from Val de Travers[2] yielded a brown crude oil which on fractional distillation gave the following results

TABLE 1

	1	2	3	4	5	6
Boiling point, degrees	90–120	120–150	150–180	180–200	200–220	220–250
Specific gravity	0 784	0 790	0 802	0 817	0 845	0 867
Carbon, per cent	87 56	87 56	87 31	87 34	87 18	87 10
Hydrogen, per cent	12 34	12 50	12 59	12 69	12 60	12 40

The results indicate that the oil was composed of hydrocarbons of the C_nH_{2n-2} series (acetylene). Similar results were obtained from the destructive distillation of an asphalt from the Dead Sea.[3]

The following results were obtained by distillation of the various asphalts at atmospheric pressure, the percentages.

TABLE 2[1]

Temperature	Trinidad, per cent off	Bermudez, per cent off	Gilsonite, per cent off	Tabbyite, per cent off	Wurtzilite, per cent off	Ozokerite, per cent off
0–150°C.	14.93	9 89	9 34	3 12	16 15	0 21
150–200°C.	10 42	7 99	5 34	11 93	21 70	8 91
200–250°C.	2 26	16 08	12 84	21 87	22 82	8 38
250–300°C.		21 12	28 99	13 21	0 91	17 69
300–350°C.				1 77		25 89
350–400°C.						26 85
Total volatile	27 61	55 08	56 51	57.90	61 58	87 93
Fixed carbon	36 69	39 60	43 13	37 15	36 92	10 03
Ash	35 70	5 32	0 36	4 65	1 50	0 04

[1] C. BARDWELL, B. A. BERRYMAN, T. B. BRIGHTON and K. D. KUHRE, *Jour. Ind. Eng. Chem.*, Vol. **5**, 1913, pp. 973–976.

Destructive Distillation of Wood.—The crude products obtained in the destructive distillation of hard and resinous woods are charcoal, vapors and gases. The charcoal is a finished commercial product containing as high as 25 per cent volatile matter. On condensation the vapors yield a pyroligneous acid and tar. The acid is composed of an aqueous solution of acetic acid, acetone, methyl alcohol, methyl acetone, aldehydes, dissolved tar and oils. The tars on treatment yield flotation oils, solvent oils, heavy tar oils for paints, preservatives

[1] K. KHARICHKOV, *Chem. Abs.*, 1910, p. 1237.
[2] C. VOLCKEL, *Ann. der Chem.*, 1853, Vol. **87**, pp. 139–148.
[3] B. DELACHANAL, *Compt. rend.*, 1883, Vol. **97**, pp. 491–494.

and insulating pitch. The oils are valuable raw materials for medicinal beechwood creosote.

The gas contains large quantities of CO_2 and its main combustible constituents are CO and CH_4. Its calorific value is low and it is ordinarily used for fuel.

From resinous woods, such as yellow pine and fir, the chief commercial products are charcoal, turpentine and tar. Hard woods, such as oak, beech and maple, yield larger percentages of alcohol and acetic acid and the resinous woods more tar and oils.

For a long time the distillation of wood was conducted without the recovery of most of the byproducts; charcoal was the main product obtained. For this purpose charcoal kilns or pits were used. The latter varied in shape and size, and the kilns were either beehive in shape or rectangular. Air was admitted directly to the kiln, and the heat necessary for the distillation of the wood was generated by the partial combustion of the charge and its distillation product.

In the modern method for dry distilling wood, whereby the byproducts are recovered, a standard type of a distillation apparatus, or retort is used. These are either horizontal or vertical. Kilns of the horizontal type may be either rectangular or cylindrical with an average charging capacity of about two cords.

Ovens of the horizontal type are much used. They are 6 ft. in diameter, 7 ft. high and vary in length. They may have a charging capacity of 4–8 cords of wood, depending on the length of the oven. They are usually set in furnaces with one firebox for two retorts. Vertical retorts generally yield a charcoal of high carbon content.

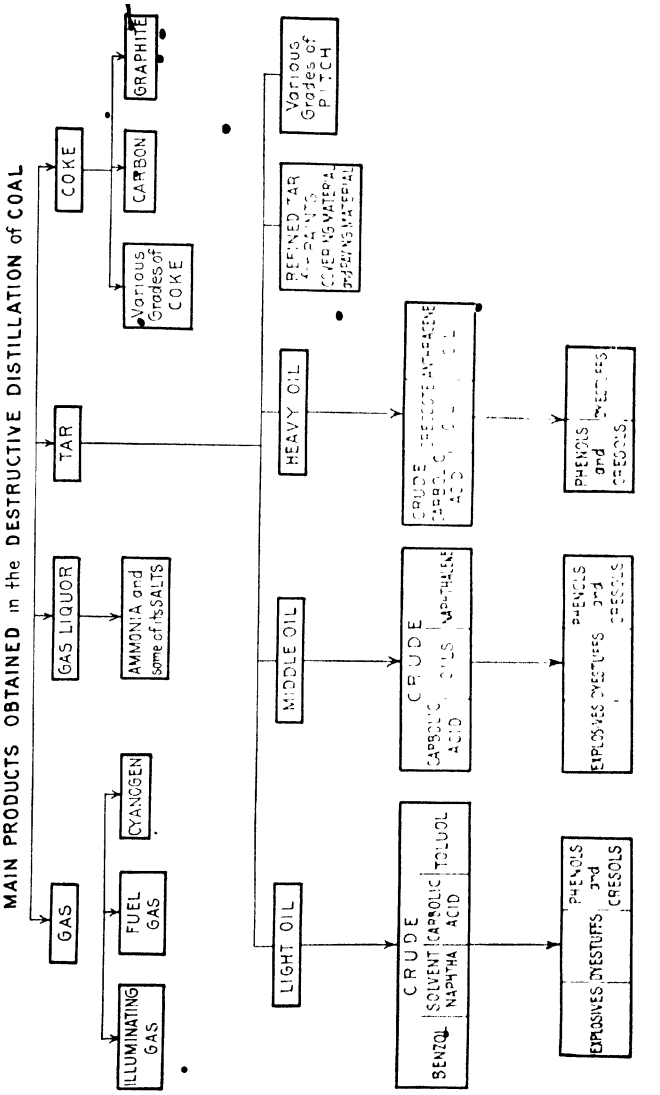
The wood is first air dried for 12–18 months; or artificially dried in much less time by the flue gases from the retort stacks. The actual operation of the distillation largely depends on the nature of the wood treated. The products obtained and their quality as well as the yield are largely influenced by the temperature employed.

The distillation of wood is an exothermic reaction. A certain amount of the wood decomposes below 270°C., largely into CO_2 and water. The exothermic reaction begins about 270°C., and the complete decomposition of wood into charcoal, vapor and gas takes place without any further addition of heat.

Two series of reactions, primary and secondary, take place in the course of the distillation. The methyl alcohol and acetic acid are among the primary products during the first decomposition of the wood. These primary products react further yielding secondary compounds. The velocity of the reaction depends on the temperature, proceeding very rapidly from 270 to 300°C. Slow distillation produces more secondary reactions because the vapors remain in the retort for a greater length of time.

The liquid resulting from the condensation of the vapors separate into two layers, the crude pyroligneous acid on the top and tar underneath. The acid layer consisting mainly of crude acetic acid is subjected to various treatments, depending on the quality of the products to be made, *i.e.*, whether brown acetate of lime or gray acetate of lime is desired. To make brown acetate of lime, the acid is neutralized with lime, and the insoluble tarry products removed. The solution is then distilled, until the wood alcohol is collected and the rest of the liquid is evaporated to dryness. To make gray acetate of lime, the crude pyroligneous acid is distilled to separate it from the dissolved tar, the distillate is neutralized with lime, allowed to settle and the clear liquid containing the wood alcohol and the oils is distilled. The acetate liquor is taken from the still and evaporated to dryness. The tar is steam distilled to remove any acid and methyl alcohol contained in it.

Destructive Distillation of Coal.—When coal is heated in the absence of air or in the presence of a limited supply, chemical reactions occur that are highly



complex and the new substances that appear in place of the coal are gas, liquid products (water and tars) and solid residue or coke. The yield and character of these products from any coal may be varied widely by changing the external conditions of temperatures, pressure, time and contact surface.

The retorts used in the destructive distillation of coal vary considerably in shape, cross-section and in length. They are set in groups or "benches" of from six to nine retorts. These may be heated by a direct fire of coke or coal, or by producer gas, which is the practice in larger and more modern plants. The retorts are arranged either horizontally or vertically and charged with from 3 to 8 tons of coal each.

In commercial practice the coking of coal is done in beehive and byproduct ovens and in gas retorts. The beehive and most byproduct ovens are used to produce metallurgical coke, whereas gas retorts are used for obtaining illuminating gas. The coke from gas retorts is not so good for smelting as from coking ovens and is usually sold for domestic fuel.

Coke is ordinarily the only product obtained when the beehive oven is used. There a semi-combustion process takes place resulting in the loss of the whole of the gas and byproducts together with part of the coke. The oven is simply a fireclay chamber, beehive shape, provided with a loose brick charging door and an exit flue. It is heated from the inside by the combustion of gases driven from the coal and of part of the fixed carbon, a limited supply of air entering through an opening in the side of the oven. Much of the volatile matter is burned inside the oven, and the remainder, which passes out through the top burns when it comes in contact with the air. In actual practice from 15–20 per cent of the coke is burned.

In byproduct ovens, coke is usually the principal product; gas, tar, ammonia, cyanides, benzol and toluol are recovered as byproducts. The byproduct retort is a rectangular chamber, measuring from 30–33 ft. in length, from 5 ft. 9 in. to 7 ft. 6 in. in height, from 17 to 22 in. in width. No oxygen comes in contact with the volatile matter to burn it and destroy the byproducts, and the latter are separated from one another in a suitable recovery system.

In gas retorts illuminating gas is the principal product, coke and ammonia being byproducts. The light oil containing benzol and toluol is left in the gas to increase its candlepower. The charges are of much smaller size than those of coking ovens.

The gases and products are drawn from the oven through cooling and washing plants for the recovery of tars, ammonia and benzol. Only one-half to two-thirds of the permanent gas is burned after the above products have been extracted. The remainder is used for heating or power purposes.

The gases are drawn from the main by the exhauster, through the cooler, either air or water cooled. In the hydraulic main the heavier tars or pitches are deposited. From the condensers the bulk of the remaining tar together with the greater proportion of the ammonia liquor is recovered.

From the condensers the gases pass into a fog extractor which removes the last traces of tar, then into the ammonia scrubber, where the last of the ammonia not recovered by the condensers is removed. From here they pass through the benzol scrubber, which is similar to that from which the ammonia is recovered. There heavy oil is used for the solution and recovery of the benzol vapors. The gas is then passed to the ovens, where it is fed into the heating flues.

The tar and ammonia liquors made in the hydraulic main condensers, tar catchers and ammonia scrubber, are collected and run into tanks. The tar settles to the bottom, the liquor remaining above the tar is run off to the ammonium-sulphate plant. There, with the aid of steam and milk of lime, mixed with the liquor, the whole of the ammonia, together with steam, hydrogen sulphide, carbonic and hydrocyanic acids, pass into a lead lined vessel, called the saturator, containing sulphuric acid. Here the ammonia is recovered as ammonium sulphate. The hydrogen sulphide and other gases pass from the saturator to the preheater, thence to a condenser, and finally into purifiers where the hydrogen sulphide is removed by oxides of iron. The crude benzol is recovered from its solution of oil by distillation.

In the Koppers byproduct-oven process, the ammonia scrubber is replaced by the sulphate saturator, thereby forming the sulphate directly in the gas main.

The processes involved in the carbonization of coal may be divided into its various steps as follows: first, liberation of primary volatile matter at low temperatures with alteration of the coal into a partly carbonized solid, second, liberation of volatile products from the altered residue by subjecting it to higher temperatures, and finally, thermal reactions among the primary volatile products. The tars and gases from the distillation of the coal are mixtures of all these different substances, most of them being secondary products.

Experimental evidence indicates that the bulk of the volatile matter of coal under proper conditions may be liberated at temperatures below 500°C. The rate at which the volatile matter distills is dependent only on the rate at which heat is supplied. More than two-thirds of the organic substance of coal is decomposed at temperatures below 500°C. (932°F.). Different kinds of coal vary in ease of decomposition.

When coal is heated it begins to evolve gaseous and liquid matter at a temperature which may be as low as 250°C. The rate of evolution gradually increases with the temperature. Above 550°C. it begins to decline. Experiments have shown that in the distillation of bituminous coal the reactions that occur in the coal at temperatures below 750°C. absorb heat, but those at temperatures above 750°C. evolve heat [1]

It is possible to control the thermal decomposition of hydrocarbons in such a way as to give maximum yields of certain products of decomposition, such as constituents of gases, aromatic hydrocarbons, etc. The factors that control these yields are temperature, pressure, length of time in the reaction zone, the starting material and catalysts.

Thermal decomposition of the volatile matter takes place very easily at temperatures above 750°C. (1,382°F.). It increases the yield of the permanent gases, hydrogen and hydrocarbons. Distillation at temperatures above 750°C. yields gases in which hydrogen predominates, whether secondary reactions are prevented or not; but secondary reactions of the volatile products will increase the total gas yield at the expense of the tar.

Paraffin hydrocarbon gases of the series C_nH_{2n+2} higher than methane predominate at temperatures below 400°C. Coals rich in oxygen (10–11 per cent) and hydrogen (above 5 per cent) and which, therefore, have large percentages of resinic bodies, on being carbonized at low temperatures yield tars rich in phenol and cresol.

Recently the nature of the liquid primary products has been determined [2] On distilling coal *in vacuo* at low temperature, 430°C., 6.5 per cent the weight of a bituminous coal was obtained as tar. Of this tar 50 per cent was a pitch residue and 50 per cent. an oil separated by distillation to 300°C. The oil consisted of 40–45 per cent ethylene hydrocarbons; 40 per cent naphthene and liquid paraffins; 12–15 per cent phenols, chiefly cresols and xylenols, 7 per cent aromatic hydrocarbons apparently homologues of naphthalene; and solid paraffin and pyridine bases in small quantity. Benzene and its homologues as well as anthracene, carbon bisulphide and solid aromatics were absent. Sulphurous gases are readily produced in the decomposition of coal. They begin to be formed at temperatures as low as 250°C. (482°F.).

The higher the heat of the distillation the larger the volume of the gas produced and the lower its quality as an illuminating agent, while the condensible tar obtained decreases in quantity, but increases in specific gravity owing to the presence of a larger proportion of heavy and high boiling constituents.

When the temperature is only slightly above that which decomposition commences, the volatile products formed consist chiefly of liquids of somewhat similar constitution

[1] H. Hollings and J. W. Cobb, *Jour. Chem. Soc.*, Vol. **107**, 1915, pp. 1106–1115.
[2] D. T. Jones and R. V. Wheeler, *Jour. Chem. Soc.*, Vol. **105**, 1914, pp. 140–151.

to those contained in petroleum oil, the gas formed being small in volume and of high illuminating power.

When the temperature is raised, the volatile products first produced undergo further changes in contact with the red-hot coke and surface of the retort. They are therefore, converted into hydrogen and simpler hydrocarbons as methane, ethylene, etc., and more complex substances belonging to the aromatic series, such as benzene, toluene, naphthalene and anthracene. As the temperature is further raised the quantity of hydrogen formed increases with simultaneous production of more and more complex hydrocarbons containing smaller percentages of hydrogen.

Low temperature favors the formation of the total light and heavy oil and tar acids and correspondingly an increase in temperature, causes a falling off in the percentage of those compounds with an increase in the percentage yields of heavy oil; a decrease in the percentage yield of paraffins; and an increase in that of the aromatics.

Diminishing the duration of the carbonization period tends to increase the actual yields of total, light and heavy oils as well as the yields of the total benzene, toluene, and xylene fractions. Slow carbonization tends to increase the yield of coke.

The factors to be considered in any coal carbonization process are as follows (1) Temperature at which carbonizing reactions take place; (2) pressure in the carbonizing retort; (3) concentration of the various constituents involved in the carbonizing reactions; (4) duration of the reactions taking place in the retort during carbonization; (5) size and character of the surfaces in contact with the constituents undergoing decomposition, or the catalytic effect; (6) nature of the coal.

TAR

Ordinary coal tar is formed from coal at high temperature, chiefly as the result of the decomposition of a tar previously formed at low temperature. The mechanism of the process consists essentially in the decomposition of the naphthenes, paraffins and unsaturated hydrocarbons present in the low temperature tar to form olefines of various carbon content which condense to form aromatic compounds. [1]

There is a variation in the composition of the tar according to the kind of retort and carbonizing temperature employed. If the coal is carbonized in chamber or vertical retorts or at low temperature, a lower gravity tar is obtained. High heat in horizontal retorts produce tar of high specific gravity. On subjecting the tar to destructive distillation about 190 definite chemical compounds can be separated from the distillates and the pitch.

Tars produced at low temperatures yield on distillation phenols of the carbolic acid series and also of a series less acid in behavior; a smaller amount of naphthalene and of the benzene hydrocarbons, a large percentage of hydrocarbons of the paraffin and olefine series; a small amount of free carbon, and most of the nitrogen in the form of aniline and its homologues.

Tars produced at high temperatures yield traces of paraffinoid hydrocarbons on distillation. The predominating hydrocarbons are those of the benzene, naphthalene and anthracene series; the nitrogen occurs principally in the form of pyridine bases; the phenols consist chiefly of carbolic acid and its homologues; the percentage of free carbon is generally high.

Tar stills are built in various sizes with a working capacity of 10, 15, 20 or 30 tons.

[1] D. T. JONES, *Jour. Soc. Chem. Ind.*, Vol. **36**, 1917, pp. 3-7.

The vertical still is most satisfactory. The amount of tar usually obtained from gas coal is equivalent to about 5 per cent of the amount of the coal.

The products of high-temperature carbonization from coal of the Pittsburgh type on an industrial scale at about 800–900°F. (427–482°C.) consist of a rich gas amounting to 0.6–0.7 cu. ft. per pound of coal, and a large yield of oil tar comprising 10–12 per cent of the coal. This tar consists chiefly of paraffin hydrocarbons, a very small amount of benzene and naphthalene derivatives and practically no carbon. The gas contains 6–7 per cent of unsaturated hydrocarbons and 20–25 per cent of ethane and its higher homologues. It will, therefore, have a high calorific and illuminating value.

The tar obtained from the distillation of paraffin base oils is in general much like a coal tar except that it contains no oxygen, nitrogen or sulphur compounds. The aromatic tars differ from coal tar in that they contain no straight chain compounds.

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SECTION XIX

REFRIGERATION

By Van Rensselaer H. Greene[1]

Theory of Refrigeration.—Refrigeration is the art of producing temperatures below the normal for useful purposes. The theory of refrigeration is based upon the flow of heat from a warm body to one that is cooler. Commercially, there are two methods possible for producing a refrigerating effect: The heat may be transferred to a cold body which is afterwards discarded, as when rooms, liquids, etc. are cooled by means of ice or a mixture of ice and salt; or a continuous mechanical refrigerating effect may be produced by means of a circulating agent which absorbs the heat, and is afterwards made to change its physical state and transfer that heat to some ordinary cooling medium such as water or the atmosphere; following which the heat-absorbing vehicle reverts to its original state again, and the cycle begins a second time; and so on *ad infinitum*.

In the field of refrigeration in this country, the unit of heat measurement is the "British thermal unit," written "B.t.u." One B.t.u. is the quantity of heat required to raise the temperature of 1 lb. of water, at or near the point of maximum density (39°F.), 1°F. One pound of ice, in melting, absorbs 144 B.t.u., and this is known as the latent heat of fusion of ice. The quantity of heat which becomes latent, due to the melting of 1 ton (2,000 lb.) of ice, is therefore 288,000 B.t.u.; and the absorption of this quantity of heat is known as "One Ton of Refrigeration."

When two solid bodies, such as ice and common salt (NaCl), mix to form a liquid, a certain amount of heat becomes latent, and as soon as the mixture takes place, the temperature of the resulting liquid falls correspondingly. With mixtures of ice and salt, this latent heat is equal to 144 B.t.u. for each pound of ice present, minus a small quantity of heat, known as the heat of solution of salt, which varies with the proportion of salt used. The temperature to be obtained from a salt and ice mixture depends principally upon the relative proportions of the mixture, but also, to some extent, upon the rate at which outside heat is supplied, and the size of the ice lumps and salt particles. On this account it is more or less impracticable to fix the exact temperature which will result from a given ratio of salt and ice. In general, however, it may be stated that with a 10 per cent mixture, by weight, of ice and salt (NaCl), a temperature of 20°F. may be obtained; with 15 per cent of salt, a temperature of 12°; with a 20 per cent mixture, 0°F.; and with 25 per cent of salt; 10° below zero. The properties of other salts, such as calcium chloride, magnesium chloride, etc., differ somewhat from those of the ordinary sodium compound. When such salts are present in quantity, therefore, these figures will not hold true.

If a mixture is made of a given amount of ice and salt, both at a temperature of 32°F., and sufficient heat is supplied to melt the ice, absorb the salt, and raise the temperature of the resulting brine to the original 32°F., the total quantity of heat absorbed in carrying out this operation will be the algebraic sum of the latent heat of the ice and the heat of solution of the salt. This heat of solution will vary with the

[1] Refrigerating engineer, 35 Warren St., New York City.

relative quantity of salt used; and the heat absorbing value of a brine of any given density, corresponding to the particular ratio of ice and salt entering into it, will be a constant quantity.

To illustrate: A 5 per cent salt mixture (NaCl) will absorb 140 B.t.u. per pound; a 10 per cent solution, 133 B.t.u.; a 16 per cent solution, 125 B.t.u.; a 20 per cent mixture, 120 B.t.u.; and a 26 per cent solution, 110 B.t.u.

When the temperature of the salt used is much above 32°F., a slight difference in these figures will result, ranging from zero to 5 or 6 per cent as the temperature of the salt is higher.

The use of salt with ice in a refrigerator does not increase the cooling effect to be obtained from a given amount of ice, but it does cause the ice to melt more rapidly, and so absorb heat more quickly. In other words, when salt is used, the melting point of the ice is lowered. But whether salt is added or not, 1 lb. of ice, in melting, only absorbs 144 B.t.u. and no more. With the addition of salt, the heat absorption is quickened; hence a lower temperature for a shorter period. There is no gain in efficiency in employing such mixtures. In fact there is a slight loss, due to the heat of solution of the salt.

Mechanical Refrigeration.—For the purposes of mechanical refrigeration, in order to produce a continuous cycle, it is necessary to provide a circulating cooling medium of such a nature, that with the aid of mechanical force, without excessive pressure, it can be made so to alter its physical state, and in so doing, to increase its temperature, that the greater part of its heat content may be discharged to the atmosphere or to ordinary cooling water.

The usual mechanical refrigerating cycle consists of two stages, as follows: (1) A vapor at low tension is mechanically compressed to a point sufficiently high to permit of its liquefaction at ordinary temperatures, and the sensible heat of the hot compressed gas is removed by flowing water in a surface condenser. This causes the gas to liquefy, and it then flows to a container adapted to store it under pressure. (2) The liquefied vapor—still a liquid—is brought into contact, under reduced pressure, with the body to be cooled. The lowered pressure and proximity of a warmer body at once cause the liquid to vaporize rapidly, and this is necessarily accompanied by the absorption of heat, which is taken from the most available source, the body which it is desired to refrigerate.

The heat absorbed, as previously explained, is called the "latent heat" of the body which absorbs it. It is defined as follows. The latent heat of a substance is the number of B.t.u. required to change the state of 1 lb. of the substance without changing its temperature, as for instance, the latent heat of vaporization of a liquid; the latent heat of melting of ice.

The circulating refrigerating medium above spoken of is known as the "refrigerant." The theoretical requirements of a good refrigerant are: (1) A low boiling point at ordinary pressures; (2) a high latent heat value; (3) a small specific volume.

A low boiling point is desirable because it makes operation possible with low pressures throughout the major part of the cycle. The latent heat of vaporization is, to a large extent, a practical measure of the cooling effect; so it is obvious that the greater the latent heat, the better the refrigerant. The volume of vapor per pound of the refrigerating medium determines the size of the machine parts.

The mediums most exclusively used in the refrigerating industry are ammonia, carbon dioxide, sulphur dioxide, ethyl chloride, and methyl chloride. Accompanying will be found a table giving the absolute pressures of these mediums at 0°F. and 95°F., and also their latent heats of vaporization.

	Absolute pressure at 0°F., pounds per square inch	Absolute pressure at 95°F., pounds per square inch	Latent heat of evaporation at 0°F.
Ammonia	29 95	197 30	572 2
Carbon dioxide	314 00	1211 00	124 4
Sulphur dioxide	9 93	77 64	172 0
Ethyl chloride	4 04	31 80	190 4
Methyl chloride	18 73	110 10	176.0

Since ammonia has a much greater heat of vaporization, and reasonably low working pressures, this agent is the one most generally used in the refrigerating industry. Further than this, ammonia is soluble in water, which makes possible the ammonia absorption process, as well as the ammonia compression process.

Accompanying (pp. 658 and 659) will be found a table giving the properties of ammonia at various temperatures and pressures.

Critical Data for Gases.—For each gas there is a temperature, above which it cannot be liquefied, no matter how much pressure is employed. This point is called the "critical temperature" for that gas. At any point below its critical temperature, any gas or vapor may be liquefied, providing it is subjected to sufficient pressure.

A gas having been cooled to a point just below its critical temperature, the pressure necessary to produce liquefaction is called its "critical pressure." As, however, under these conditions, the exact point of transition from one state to the other is most difficult to recognize, such determinations must always be regarded as merely approximate.

The "critical volume" of a gas is its volume at the critical temperature and pressure, as compared with its volume a 32°F, under a pressure of one atmosphere taken as a unit (normal pressure and temperature, N.P.T.).

Below will be found a table giving the accepted critical temperatures, pressures, and volumes of the gases employed as refrigerating agents.

	Critical pressure, atmospheres	Critical temperature, degrees Fahrenheit	Critical volume, calculated
Ammonia	115	266	0 00482
Carbon dioxide	77	88	0 0066
Sulphur dioxide	79	312	
Ethyl chloride	54	360 5	
Methyl chloride	73	286 9	

Rating of Refrigerating Machines.—A refrigerating machine is rated according to the number of "tons" of refrigerating effect it is capable of producing in 24 hr. at a given pressure range, and with a given temperature of condensing

PROPERTIES OF ANHYDROUS AMMONIA

Temperature, degrees		Pressure pounds per square inch		Saturated vapor		Liquid	
Fahrenheit	Absolute	Absolute	Gage	Specific volume cubic feet per pound	Density pounds per cubic foot	Density pounds per cubic foot	Latent Heat of evaporation
−10	450	23 30	8 60	11.63	0 0860	41.46	579.9
− 9	451	23 90	9 20	11 35	0.0881		579.1
− 8	452	24 52	9 82	11.08	0 0903		578.4
− 7	453	25 15	10.45	10 82	0 0924		577.6
− 6	454	25.80	11.10	10.57	0 0946		576.8
− 5	455	26 46	11.76	10.32	0 0969	41.25	576.1
− 4	456	27 13	12 43	10.08	0 0992		575.3
− 3	457	27 82	13.12	9.85	0.1015		574.6
− 2	458	28 52	13 82	9 62	0.1039		573.8
− 1	459	29 23	14 53	9 40	0.1064		573.0
0	460	29 95	15 25	9.19	0.1089	41 04	572.2
1	461	30 69	15.99	8.98	0 1114		571.4
2	462	31.44	16.74	8.78	0.1139		570.7
3	463	32 21	17.51	8 58	0.1165		569.9
4	464	32 99	18 29	8 39	0.1192		569.1
5	465	33 79	19 09	8 20	0.1219	40 83	568.3
6	466	34 60	19 90	8.02	0.1247		567.5
7	467	35 43	20.73	7 84	0 1275		566 7
8	468	36 28	21.58	7 67	0 1304		565.9
9	469	37.14	22 44	7 50	0 1333		565 2
10	470	38 02	23 32	7 34	0.1363	40 61	564 4
11	471	38 93	24 23	7 18	0.1393		563.6
12	472	39 84	25.14	7 02	0.1424		562.8
13	473	40.77	26 07	6 87	0 1455		562.0
14	474	41 71	27 01	6 72	0.1487		561 2
15	475	42 67	27 97	6.583	0 1519	40 39	560.4
16	476	43 65	28 95	6 444	0.1552		559.6
17	477	44 65	29 95	6 308	0 1585		558.8
18	478	45.67	30 97	6 176	0.1619	. ..	558 0
19	479	46.70	32 00	6 047	0.1654		557.1
20	480	47.75	33.05	5 920	0 1689	40 17	556 3
21	481	48 82	34 12	5.796	0 1725	. .	555.5
22	482	49 91	35 21	5 676	0 1762	..	554.7
23	483	51 02	36 32	5 560	0 1799	.. .	553 9
24	484	52 15	37 45	5.447	0 1836	. .	553 1
25	485	53 30	38 60	5 336	0 1874	39 95	552.2
26	486	54 47	39 77	5 228	0.1913	.	551.4
27	487	55 66	40 96	5.122	0 1953	. . .	550.6
28	488	56 87	42 17	5.019	0 1993	. .	549.8
29	489	58.10	43 40	4 918	0 2034	.	549.0
30	490	59 35	44 65	4 820	0 2075	39 72	548.1
31	491	60.62	45 92	4.724	0 2117		547 3
32	492	61 91	47 20	4.631	0 2159		546.5
33	493	63 22	48 92	4 540	0 2203		545.6
34	494	64 55	49 85	4 451	0 2247	...	544.8
35	495	65 91	51 21	4 364	0 2292	39 50	543 9
36	496	67.29	52 59	4.279	0 2337		543 1
37	497	68.69	53 99	4.196	0 2384	. ..	542.2
38	498	70.11	55 41	4.115	0 2431	. .	541.4
39	499	71 56	56 86	4 036	0 2478	.	540.5
40	500	73.03	58.33	3 959	0 2526	39.27	539.7
41	501	74.53	59 83	3.884	0 2575	...	538 8
42	502	76.05	61 35	3 810	0 2625		537.9
43	503	77.59	62 89	3.738	0.2675	.. .	537 1
44	504	79.16	64.46	3.668	0 2727	.	536.2
45	505	80.75	66 05	3 599	0 2779	39 04	535.3
46	506	82 37	67 67	3.532	0 2832	. ..	534.5
47	507	84 01	69 31	3.466	0 2885		533 6
48	508	85 68	70 98	3.402	0 2940		532.7
49	509	87.37	72 67	3 339	0 2995		531.8
50	510	89.09	74 39	3 278	0 3051	38.81	531 0

water. The usual rating is based on a suction pressure of 15.65 lb. above atmosphere, a discharge pressure of 185 lb. above atmosphere. and sufficient condensing water at 60°F.

Refrigerating machines are sometimes listed in terms of their ice-making capacity. This rating, however, should be used with great caution, as it is apt to vary widely—sometimes as much as 15 per cent—depending upon the temperature of the water to be frozen, and other variables.

Temperature, degrees		Pressure pounds per square inch		Saturated vapor		Liquid	
Fahrenheit	Absolute	Absolute	Gage	Specific volume cubic feet per pound	Density pounds per cubic foot	Density pounds per cubic foot	Latent heat of evaporation
51	511	90.83	76 13	3.219	0 3107		530.1
52	512	92 59	77 89	3 161	0 3164		529.2
53	513	94 38	79 68	3 104	0 3222		528.3
54	514	96 19	81 49	3 048	0.3281		527.4
55	515	98 03	83 33	2 992	0 3342	38 57	526.5
56	516	99 90	85 20	2 938	0 3404		525.6
57	517	101 8	87.10	2 885	0 3467		524.7
58	518	103 7	89 00	2 833	0 3530		523.8
59	519	105 7	91 00	2 783	0 3594		522.9
60	520	107 7	93 00	2 734	0 3658	38 33	522.0
61	521	109 7	95 00	2 686	0 3723		521.1
62	522	111 7	97 00	2 639	0 3790		520.2
63	523	113 8	99 10	2 592	0 3858		519 3
64	524	115 9	101 20	2 547	0 3927		518 4
65	525	118 1	103 40	2 503	0 3996	38 09	517 5
66	526	120 3	105 60	2 460	0 4066		516.5
67	527	122.5	107 80	2 418	0 4136		515 6
68	528	124 7	110 00	2 377	0 4207		514.7
69	529	126 9	112 20	2 336	0 4280		513.7
70	530	129 2	114 50	2 296	0 4354	37 85	512 8
71	531	131 5	116 80	2 257	0 4430		511.9
72	532	133 9	119 20	2 219	0 4506		511.0
73	533	136 3	121 60	2 182	0 4583		510.0
74	534	138 7	124 00	2 145	0.4662		509.1
75	535	141 1	126 40	2 109	0 4742	37 60	508.1
76	536	143 6	128 90	2 074	0 4823		507.2
77	537	146 1	131 40	2 039	0.4905		506.2
78	538	148 7	134 00	2 005	0 4988		505.3
79	539	151 3	136 60	1.972	0 5071		504 3
80	540	153 9	139 20	1 940	0 5155	37 35	503.4
81	541	156 5	141 80	1 908	0 5241		502.4
82	542	159 2	144 50	1 877	0 5328		501.4
83	543	161 9	147 20	1 847	0 5416		500.5
84	544	164 6	149 90	1 817	0 5504		499.5
85	545	167 4	152 70	1 788	0 5594	37.10	498.5
86	546	170.2	155 50	1.759	0 5685		497.5
87	547	173 0	158 30	1 731	0.5777		496.5
88	548	175 9	161 20	1.704	0 5869		495.5
89	549	178 8	164 10	1 677	0 5964		494 5
90	550	181 8	167 10	1 650	0 6060	36 84	493.5
91	551	184 8	170 10	1 624	0 6158		492.5
92	552	187 8	173 10	1 598	0 6258		491 5
93	553	190 9	176 20	1.573	0 6358		490.5
94	554	194 1	179 40	1 548	0 6460		489.5
95	555	197 3	182 60	1.524	0 656	36 58	488.5
96	556	200 5	185 80	1 500	0 667		487.5
97	557	203.8	189 10	1 477	0 677		486.5
98	558	207 1	192 40	1 454	0 688		485.4
99	559	210 4	195 70	1 431	0 699		484.4
100	560	213 8	199 10	1 408	0 710	36 32	483.4

Measurement of Refrigerating Effect.—The commercial unit of refrigeration is the "ton of refrigeration," before spoken of. This term is used to designate the number of B.t.u. required to melt (not manufacture) one ton of 2,000 lb. of pure solid ice. Since the latent heat of ice is 144 B.t.u., 1 ton of refrigeration is equal to 144 B.t.u. multiplied by 2,000, or 288,000 B.t.u. All refrigerating machinery calculations are based on a 24-hr. day, and refrigerating capacities are figured at the rate of 12,000 B.t.u. per hour, or 200 B.t.u. per minute.

Refrigerating Systems.—There are two commercial systems of refrigeration in use. They are known as the "compression system" and the "absorption system." The compression system is suitable for use with any of the refrigerating mediums listed in this section, and doubtless could be used with others not yet discovered. The absorption system, on the other hand, is distinctly an ammonia system. Due to its greater flexibility, the majority of the refrigera-

ting plants in use operate by the compression system. Both of these systems require water to extract the heat from the refrigerating medium.

Compression System.—The ammonia-compression system of refrigeration depends upon the mechanical compression of ammonia vapor, so that the resulting gas may be liquefied, and its heat content removed, after which it is vapor-

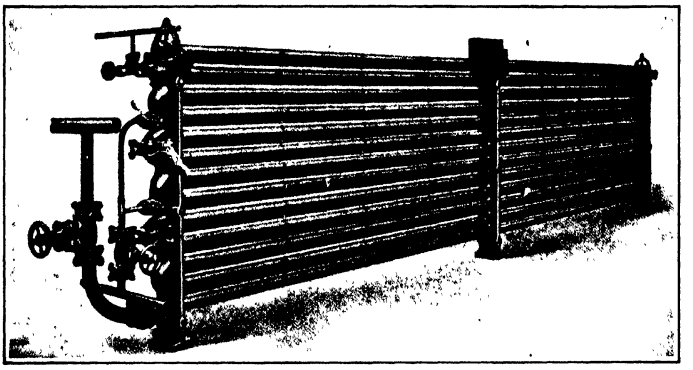


FIG. 1.—Atmospheric condenser.

ized again in contact with the objects to be cooled. The principal pieces of apparatus required are as follows: The compressor; the condenser; the liquid receiver; and the expansion coils. These, with the addition of the various pipe connections and lesser appurtenances, make up the entire plant.

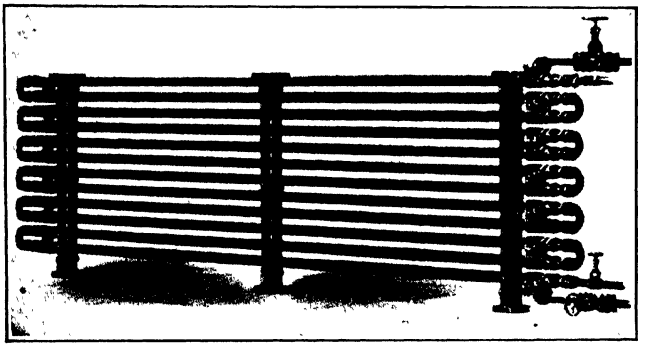


FIG. 2.—Double pipe condenser.

The compressor is a machine much like an air compressor, and is driven in the same manner. With regard to speed, compressors are of two general types: low-speed machines, and high-speed machines. The former run at about 75 r.p.m., and the latter at about 225 r.p.m. The function of the compressor is to compress the ammonia gas.

The condenser is a coil of pipes for condensing the compressed ammonia gas, the gas being usually passed through the inside of the pipes, while water is applied externally.

Condensers are of two principal types: The "atmospheric" condenser, and the "double pipe" condenser. The purpose of the condenser is to remove the heat from the compressed vapor, and so cause it to change its state from a gas to a liquid.

Figure 1 shows the "atmospheric" type of condenser. It is usually constructed of 2-in. wrought-iron pipe, 12 pipes high, and 20 ft. long. This type of condenser is best located in the open air, on the roof of a building, or in some other exposed place. When in operation, the compressed ammonia passes through the pipes, while the cooling water trickles down over the outside. There is no economy in making these condensers more than 12 pipes high.

The double-pipe condenser, shown in Fig. 2, consists of two concentric pipe coils put together with suitable composite end fittings. The ammonia gas is passed through the outer annular space, while the cooling water circulates through the central pipe.

The liquid receiver, Fig. 3, is a cylindrical drum, which is used as a reservoir for the storage of the liquid refrigerating medium, in this case, ammonia. The

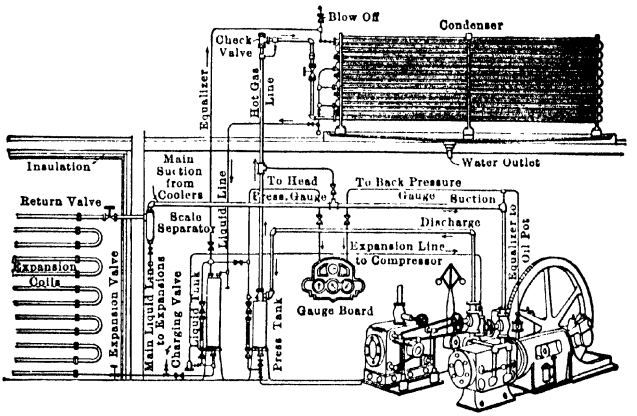


FIG. 3.—Compression side ammonia refrigeration system.

expansion coils are pipe coils, which are located in the rooms or other places where a cooling effect is desired. The refrigerated medium is circulated through these coils, which are usually constructed of 1¼- or 2-in. pipe.

The cycle of operation of an ammonia compression system, such as that shown in Fig. 3, is as follows: The ammonia gas enters the compressor, or ice machine, as it is called, at a low pressure, say 15 lb., and is there compressed to, say 185 lb. As the gas is compressed, its temperature also rises. It is then passed through an oil separator, which removes the oil absorbed while going through the compressor, after which it flows to the condenser. Here, the cooling water, which is sprayed over the outside of the condenser pipes, removes enough heat from the compressed vapor to cause it to condense to a liquid. The anhydrous liquid ammonia thus formed then flows to the liquid receiver. This much of the system is known as the high-pressure side.

The liquid ammonia is then released, through an expansion valve, into the expansion coils; and as it passes through this valve, the pressure upon it automatically drops from 185 lb.—the condenser pressure—to 15 lb.—the suction pressure maintained by the ice machine, with which the expansion coils are in direct connection. This drop in pressure carries with it a drop in temperature from 95 to 0°F., and the cold liquid in

the expansion coils, being wholly unconfined, boils away to a gas, absorbing heat from everything in its neighborhood. The gas is then returned to the compressor, completing the cycle of operation.

In the practical operation of a system of this kind, the discharge pressure is necessarily governed by the temperature and amount of the available condensing water, while the suction pressure on the machine must be maintained by the operator at the point required to produce the desired temperature in the rooms. Assuming a 15° difference in temperature between the cooling medium and the air in a room, if it is desired to keep this room at 15°F., the temperature of the ammonia must be 0°F. By referring to a table of the properties of saturated ammonia, it will be found that 0°F. corresponds to a pressure of 15.25 lb. The machine, therefore, should be operated at this back pressure. When the expansion valve is once properly set to pass the required quantity of ammonia to the expansion coils, the entire system may be controlled by operating the compressor so as to maintain this suction pressure.

The chief advantages of the system are two in number: (1) Steam is not necessary. An ammonia compressor and all needed auxiliaries may be operated by gas engine, oil engine, or electric motor, none of which require a boiler. (2) All the apparatus is extremely efficient and economical to operate. Therefore, low production costs are always possible, wherever power is to be had at reasonable cost.

The principal disadvantage of the system lies in the fact that temperatures below about 0°F. cannot usually be maintained with a single-stage compressor without an excessive expenditure of power. On this account, in the past, recourse has been had to the absorption machine, whenever excessively low temperatures were needed. At the present time, however, high-class two-stage compressors are available, which are very efficient and economical. A machine of this type, recently installed by the writer in Philadelphia, keeps a tier of hardening rooms at the factory of the Colonial Ice Cream Co. at −16°F., day and night without difficulty.

Two-stage Compression.—In refrigerating plants, the value of two-stage compression lies in the possibility which it presents of carrying very low back pressures. This most attractive feature would have led, no doubt, to the general adoption of two-stage compression long ago, but for the difficulties attending its use, due to the want of a suitable method of inter-cooling between stages. In the ammonia machine of this type, operating at a very low back pressure, the compressed ammonia coming from the first stage is still quite cool, and the temperature of the gas in the inter-cooler cannot be successfully controlled by ordinary water, usually warmer than the gas itself. It therefore becomes necessary where cool water is not available to find some other means of heat regulation, and the method which immediately presents itself is by the injection of liquid ammonia into the partially compressed gas.

This is the method of inter-cooling used in the modern two-stage compressor. Special precautions, however, must be adopted to obviate the great danger which attends this practice, due to the fact that the liquid ammonia is apt to carry over—still a liquid—into the second-stage cylinder, and blow out the head of the machine.

Two distinct methods are in use for avoiding this danger. In one—the most successful—a supplementary container, filled with helical pipe coils nested together, is placed just below the inter-cooler; and the surplus ammonia injected into the inter-cooler, in excess of that needed for the inter-cooling of the partially compressed gas, flows into it by gravity. Through these helical pipe coils, the entire anhydrous ammonia supply of the plant is made to pass, its temperature being comparatively high—about that of the ammonia condenser. So the surplus ammonia from the

inter-cooler, being brought in contact with this great mass of warm liquid, expends itself in cooling it, at the same time boiling away to a gas. In this way it is made to do useful work in the refrigerating cycle, and the danger above described is entirely eliminated.

The second method used is to allow the surplus ammonia to drain out of the inter-cooler to the suction of an ammonia pump, which discharges this liquid directly back into the high-pressure feed lines. This, however, is not so reliable as the method first described, as there is a possibility of the ammonia pump becoming gas bound, and more or less difficulty in keeping the pump suitably packed to handle the cold liquid.

Tonnage of Ammonia Compression Machines.—As refrigerating effect is produced by the vaporization of a liquid into a gas, the capacity of a refrigerating machine is measured by its ability to handle a given number of cubic feet, per minute, of the gaseous refrigerant. From the ice-machine-builder's standard, approximately 5 cu. ft. of ammonia gas per minute, compressed by a given machine under standard conditions, is the practical equivalent of one ton of refrigerating effect per day of 24 hr.

Under normal conditions, the water used to condense the compressed ammonia is obtained from the city mains; and in the summer months, its temperature is in the neighborhood of 75°F. With water at 75°F. showered over the ammonia condensers, the head pressure on the machine, set by the temperature of liquefaction of the gas, will be somewhere between 155 and 185 lb., depending upon the design and efficiency of the condenser employed.

Manufacturers of refrigerating machines have adopted as their standard for rating purposes a condenser or head pressure of 185 lb., and a suction pressure of 15 lb.; so that the compression of 5 cu. ft. of gas per minute, from a suction pressure of 15 lb.; to a condenser pressure of 185 lb., represents an ice-machine capacity of 1 ton of refrigeration per 24 hr.

Horsepower of Ammonia Compressors.—Under these conditions, the compression of 5 cu. ft. of ammonia gas per minute will require, theoretically, 1½ horsepower, expended in the cylinder of the compressor, exclusive of the friction losses of the compressor itself, the friction losses of the steam engine which drives it (if any), and the belt friction, if a belt is used. These various losses, in the aggregate, will amount to about 15 per cent, giving a total expenditure of power, per ton of refrigeration, of 1¾ hp.

Ice-making Capacity of Compression Machines.—When ammonia-compression machines are used for making ice, they are called upon not only to remove the latent heat of freezing from the water, but also to cool the water itself from its initial temperature down to 32°F., and the ice, after it has been frozen, from 32°F. down to the temperature of the freezing tank; and besides all this, to replace all heat leakage from the various piping, and from the brine tank itself, with its great charge of ice still being frozen in the cans. These various losses, taken together, amount to fully 40 per cent of the latent heat of freezing, so that an ammonia compressor must compress at least 7 cu. ft. of gas per minute for every ton of ice to be manufactured by it per day of 24 hr. The total expenditure of of power, per ton of ice manufactured per 24 hr., will be 2.45 hp. for 24 hr., or 58.8 hp.-hr.

Absorption System.—The ammonia-absorption system is based upon the great solubility of ammonia gas in water, which, at ordinary temperatures,

is about 700 volumes of the gas to one volume of water. The apparatus required consists of the generator, the rectifier, the exchanger, the condenser, the liquid receiver, the expansion coils, and the absorber; together with the necessary pump, some minor apparatus, and the pipe connections. Ammonia is the only refrigerant adapted for commercial use with an absorption system. No other cheap medium is sufficiently soluble.

The expansion coils, condenser, and liquid receiver used in this system are identical with the apparatus similarly named for use in compression plants. They also perform the same functions, and have the same relation to each other. In the compression system, the compressor is the main energizing unit or heart of the plant. In the same way, the absorber is the heart of the absorption system.

The ammonia absorber is a cylindrical drum, much like a horizontal tubular boiler, with interior tubes parallel to its longitudinal axis, terminating in tube sheets located near each end. Cooling water is passed through the tubes to cool the mixture of water

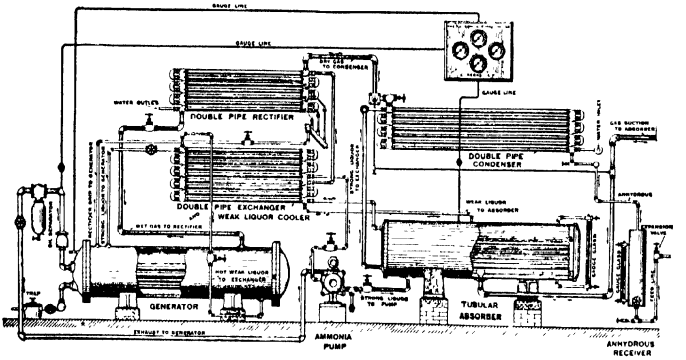


FIG. 4.—Ammonia absorption plant.[1]

and ammonia in the shell surrounding them. A very weak mixture of water and ammonia, termed weak liquor, continually flows into the absorber from the exchanger —a piece of apparatus to be described later on. Spent ammonia gas from the expansion coils is led into the bottom of the absorber through a perforated pipe, and caused to bubble up through the liquor contained in it. This weak liquor rapidly absorbs it, and thus enriched by the addition of ammonia gas, now becomes what is called strong liquor. A stream of this strong liquor is continually pumped out of the absorber by a horizontal steam-driven piston pump called the ammonia pump, which is the only moving piece of apparatus required.

From the pump, the strong liquor flows through a set of double pipe coils, spoken of above, called the exchanger. Here, the cold strong liquor in one pipe, which has just left the absorber, picks up some of the heat from the hot weak liquor in the other pipe, coming back from the generator to the absorber. In this way the strong liquor is warmed to some extent, and then passes on to the generator.

The generator is another cylindrical drum, which has a set of steam coils suspended in it. Steam, at a pressure of from 10 to 20 lb., furnished from the exhaust of the ammonia pump or from other sources, is made to pass through these coils, to heat the strong liquor with which the shell of the generator is filled. The greater part of the ammonia in this strong liquor, and some of its water, is in this way vaporized, forming a hot wet gas, which flows away from the generator, leaving a hot weak liquor behind.

[1] Courtesy Carbondale Machine Co., Carbondale, Pa.

The ammonia gas driven out of the liquor produces a head pressure in the interior of the generator; and, impelled by this, a continual stream of the hot weak liquor flows away, passing first through the exchanger, as before mentioned, and then through a weak-liquor cooler, which is another set of double pipe coils, cooled by running water. From this point, the weak liquor flows back to the absorber, as described in the first paragraph, completing that cycle of operation.

The hot wet ammonia gas, escaping from the generator, is first led to the rectifier, a series of pipe coils arranged with drip connections on several of the pipes. Cold water is passed over the coils of the rectifier, to condense the water vapor in the ammonia gas, and the condensed water, thrown down in this way, is drawn off through the various drips, and led back to the generator. The warm ammonia gas, now freed from moisture, passes on to the condensers, and from there to the liquid receiver, where it is stored in the form of anhydrous liquid ammonia, ready for use in the expansion system as it is needed. Later on, the spent expanded gas coming from the refrigerating coils, is led back to the absorber, completing that cycle of operation.

Figure 4 is a diagram showing the various pieces of apparatus, and the two cycles of operation, in the ammonia absorption system. The control of the entire process is in the speed of the ammonia pump, which must be regulated by the operator to take care of the demands made upon the plant from time to time.

The advantages of this system are three in number: Simplicity of control; the fact that exhaust steam can be utilized; and the fact that very low temperatures are possible. Little attention, as a rule, is required on the part of the operator; and the possibility of using exhaust steam is often an important factor. With plants of this character, room temperatures as low as 20° below zero can be obtained.

The principal disadvantages of plants of this kind are. (1) That steam is an absolute necessity; (2) that the thermal efficiency of the process is low; (3) that the system is rather inflexible, requiring to be operated at a fairly constant rate.

Ammonia Not the Only Practical Refrigerant.—While ammonia, on account of its high heat of vaporization and low working pressure, is the refrigerant generally employed in a commercial way, a number of other agents are in use to a greater or less extent. The mode of operation with these other liquids is practically similar to that of the ammonia-compression system; and the machines and other appliances are, in a general way, the same. In this class will be found compression plants utilizing carbon dioxide, sulphur dioxide, Pictet liquid, ethyl ether, ethyl chloride, and methyl chloride.

Refrigeration may also be accomplished by means of the compressed-air refrigerating machine; vacuum machines, both simple and compound, and by the evaporation of liquefied air and other gases.

The Carbon-dioxide Machine.—Refrigerating machines employing carbon dioxide as a refrigerant have been used more or less in the past for particular cases, where it was feared that leaks might occur, and the contents of the storage rooms damaged, if ammonia machines were installed. Among the advantages claimed for this process are the fact that the agent cannot be decomposed by compression, it is absolutely non-corrosive, and but slightly poisonous. On the other hand, it must be remembered that carbon dioxide is inodorous, and leaks might exist for long periods without being discovered.

Below will be found a table giving the properties of carbon dioxide. In making calculations, however, it should be remembered that the gas is in a superheated condition during an appreciable part of the refrigerating process, and due allowance made for the variations which will occur on this account.

PROPERTIES OF CARBON DIOXIDE

Boiling point, degrees Fahrenheit	Absolute pressure, pounds per square inch	Total heat of gas above 32°F.	Heat of liquid above 32°F.	Latent heat of evaporation	Heat equivalent of external work	Weight of 1 cu. ft. vapor, pounds
−22	210	98.34	−37.80	136.15	16 20	2.321
−13	249	99 14	−32 50	131 64	16 04	2.759
− 4	292	99.87	−26 90	126.78	15.80	3.265
5	341	100.57	−20 92	121.50	15 50	3.852
14	396	101.20	−14.50	115.70	15.07	4.535
23	457	101.80	− 7.56	109.38	14.58	5.330
32	525	102 35	0.00	102 35	13.94	6.265
41	599	102 85	8.32	94.52	13.14	7.374
50	680	103 24	17.60	85.64	12.15	8.708
59	767	103.58	28 22	75 37	10 91	10.355
68	864	103.83	40 86	62 99	9 29	12.480
77	968	103.95	57 05	46 88	7 06	15.474
86	1080	103 72	84 45	19 28	2 96	21.520

Construction of the Carbon-dioxide Plant.—Plants of this type are built much the same as the ammonia-compression plant, consisting mainly of a compressor, a condenser, and an evaporator or refrigerator, where the compressed and liquefied refrigerant is evaporated to absorb heat. The compressor may be either horizontal or vertical, but must be built extremely strong. It is generally provided with an external jacket through which the suction gas passes, this arrangement giving additional strength, while, at the same time, it tends to keep the compressor cool. These compressors generally operate at a piston speed of about 2 ft. per second; and the suction valve has an area somewhat less than half the area of the piston, while the discharge valve is about one-fourth of that. The piston rod is usually packed with leather cups, glycerin being continually forced into the spaces between the leathers, so that any tendency to leakage simply results in some of the glycerin being drawn into the cylinder or forced out into the air, and no escape of gas is ever possible. A belt-driven pump is generally used to keep up the glycerin pressure.

Any surplus glycerin which passes into the machine, beyond that needed to fill up the clearances, is forced out with the gas through the discharge valves; and a trap is provided to separate it from the hot gas on its way to the condenser, and return it to the glycerin pump, so that it may be used again and again.

The condenser is generally constructed of extra-heavy wrought-iron pipe, much like an ammonia condenser, but stronger. It may be submerged in a cooling tank, or arranged for the showering of water over it, as is done with the atmospheric ammonia condenser. In the best practice, the coils are welded together; and in some cases, it has been found beneficial to have them constructed of copper; which is possible with this gas, on account of its non-corrosive character.

The evaporating system (or expansion coils) used with carbon-dioxide plants, is usually constructed of extra-heavy wrought-iron pipe with welded joints. Either direct expansion or the brine system may be used, but, for most purposes, the former is preferred. All joints should be made up with the highest class of brass-bushed flange unions, with gaskets of vulcanized fibre or other material, which, while sufficiently elastic to insure tightness, will not deteriorate with the constant heat.

The working pressures vary between 50 and 75 atmospheres, but as these compressors—even in the largest sizes—have very small diameters, no difficulty is experienced in providing an ample factor of safety in all parts. In designing such machines, a factor of safety of at least three times the highest working pressure which will come upon it should be provided for each piece.

Another advantage of this mode of refrigeration besides those given lies in the cheapness of the agent used. Cheap liquefied carbon dioxide is now manufactured as a by-product of the brewing industry in Europe. The gas has no effect on any of the metals, and is inert to nearly all substances.

Among the disadvantages may be mentioned the fact that the gas is inodorous, and negatively poisonous; for, being heavier than air, it will settle in confined spaces, and produce death by suffocation, due to the exclusion of oxygen. Further than that, the working pressures are extremely high, and the system is rather inefficient, due to the high specific heat of the liquid.

The Sulphur Dioxide Refrigerating Plant.—Machines of this type are also in use to some extent. For a given amount of refrigeration, however, they must be practically three times as large as an ammonia compressor to do the same work. For low refrigerating temperatures, their efficiency, also, is low. The compressor is built much like an ammonia compressor, except that there is no need of lubricating devices.

PROPERTIES OF SULPHUR DIOXIDE

Boiling point, degrees Fahrenheit	Absolute pressure, pounds per square inch	Total heat of gas above 32°F.	Heat of liquid above 32°F.	Latent heat of evaporation	Heat equivalent of external work	Weight of 1 cu. ft. vapor, pounds
−22	5 56	157.43	−19.56	176 99	13 59	0.076
−13	7.23	158 64	−16.30	174 95	13 83	0.097
− 4	9 27	159 84	−13.05	172.89	14 05	0 123
5	11.76	161 03	− 9 79	170.82	14 26	0.153
14	14.74	162.20	− 6.53	168.73	14 46	0.190
23	18.31	163 36	− 3.27	166.63	14 66	0.232
32	22.53	164 51	0.00	164 51	14 84	0.282
41	27.48	165.65	3 27	162 38	15 01	0.340
50	33.25	166.78	6 55	160 23	15 17	0.407
59	39 93	167.90	9 83	158 07	15 32	0.483
68	47.61	168.99	13 11	155 89	15 46	0.570
77	56 39	170 09	16.39	153 70	15.59	0.669
86	66 36	171.17	19 69	151.49	15.71	0.708
95	77.64	172.24	22.98	149.26	15.82	0.906
104	90.31	173.30	26 28	147.02	15.91	1.046

The stroke is usually at least twice the diameter of the piston, which is arranged to move with a velocity of from 4 to 5 ft. per second, while the compressor valves have an area of about one-twelfth of that of the piston. In designing machines of this type, great care must be taken to insure tight joints, as any leakage of the gas is liable to result in the production of sulphuric acid, very destructive to nearly all metals.

The principal advantage in the use of this refrigerant is, that, in its liquid state, it is an extremely good lubricant, for which reason no cylinder lubricators, oil separators, or rectifiers are required. The condensing pressure, also, is quite low. The disadvantages are the necessarily large compressor, a lower efficiency, and the extreme precautions needed to prevent leakage.

Pictet Liquid.—This compound, which has also been used to some extent in compression refrigerating machines, is either a mixture or a chemical combination of carbon dioxide and sulphur dioxide, or both. Pictet, who is responsible for its introduction, claims that it is a chemical compound, corresponding to the formula CO_4S. As its behavior and temperature upon being compressed are quite different from either of the gases entering into its formation, there is some reason for believing that this is true. No exact and reliable information, however, is available with regard to the characteristics of this gas, and reports from experiments made by different investigators are, to say the least, rather conflicting. Before any definite decision can be reached as to the efficiencies to be expected from any of these compound refrigerants, further investigation should be made of their physical and chemical characteristics, and particularly, of their thermochemical behavior.

PRESSURE AND TEMPERATURE OF PICTET LIQUID

Temperature, degrees Fahrenheit	Absolute pressure in atmospheres	Temperature, degrees Fahrenheit	Absolute pressure in atmospheres
−22	0.77	50	2 55
−13	0.89	59	2.89
− 4	0.98	68	3.04
− 2.2	1.00	77	3.29
5	1 18	86	4 54
14	1 34	95	5.50
23	1 60	104	5.27
32	1.83	113	6 03
41	2 20	122	6 68

Sulphuric-ether Machines.—In former years, many compression machines were built with sulphuric ether $(C_2H_5)_2O$, di-ethyl ether, as the refrigerant. The great size of the compressor required, however, and the high inflammability of the ether itself, have caused this form of plant to be practically wholly abandoned. The size of a compressor to handle sulphuric ether is necessarily about 17 times as large as an ammonia machine of the same capacity, and the two agents are governed by the same formula, with different values for the constants, of course. One exception to this exists, however. Ether vapor superheats

during expansion, and cools during compression; just the opposite of the behavior of ammonia, steam, carbon dioxide, and sulphur dioxide. Ether compressors, therefore, are never troubled by superheat, and always handle dry vapor.

PROPERTIES OF SATURATED ETHER VAPOR

Temperature, degrees Fahrenheit	Pressure in pounds per square inch	Heat of the liquid Btu	Total heat Btu	Heat of vaporization, Btu	Heat equivalent of internal work Btu	Heat equivalent of external work Btu	Specific volume	Weight in pounds of 1 cu ft.
32	3 54	0 00	376 00	376 00	345 80	30 20	1 278	0.048
50	5.51	21.28	393 76	372 48	341 48	31 00	0 844	0 073
68	8 31	32 80	411 12	368 32	336 52	31 80	0 574	0.107
86	12 20	61 56	428 00	363 14	330 88	32 56	0 401	0 154
104	17 46	86.12	444 14	357 92	324 60	33 32	0 287	0.232
122	24 32	88.76	460 44	351.68	317 64	34 04	0 210	0. 294
140	33 17	131 20	476 00	344 80	310 12	34 68	0 158	0 392
158	44 32	153 92	491 12	337 20	301 96	35 24	0 120	0 515
176	58 13	176.84	505 76	328 92	293 28	35 64	0 093	0.705
194	74.96	200 00	520 00	320 00	284 12	35 68	0 073	0.848
212	95.25	223 44	532 76	310 32	274 48	35 84	0 057	1.074
230	119 51	247 08	547 12	300 04	264 52	35 32	0 045	1.350
248	148.44	270 96	560 00	289 04	254 28	34 76	0 036	1.703

Ethyl Chloride.—A machine utilizing ethyl chloride as a refrigerant has been on the market for some years. As the boiling point of this medium is high, the apparatus works under a vacuum, and the maximum condensing pressure is only about 15 lb. gage pressure. In a plant of this kind in Chicago, the expansion coils were made of copper, ovoid in cross-section, the section being about 4 or 5 in. wide and about 1 in. high. This type of machine has been often used in small plants for butcher shops, restaurants, etc., but is hardly of any utility for larger establishments. Its use is indicated for small experimental installations.

Methyl Chloride.—To avoid some of the disadvantages of ethyl-chloride refrigeration, the use of methyl chloride has been proposed, and for some time past, information has been published in regard to a plant of this type installed in an ice manufactory in Algiers. A 30-hp. engine is said to be used, and the plant is declared to work efficiently and smoothly with a brine temperature of 4°F. Details as to the amount of ice produced, however, and the cost of manufacture, have not been furnished.

Air Refrigerating Machine.—This form of refrigerating machine is a practical exemplification of the art of cooling by converting the superfluous heat into work. By this method, atmospheric air is compressed into a strong cylinder, provided with cooling coils, through which water is circulated to carry off the heat of compression. The compressed air is then used to drive an engine, whereupon its temperature necessarily falls in proportion to the work done by it in the engine. The air refrigerated in this way is then discharged into the rooms to be cooled, which are also ventilated by it at the same time. The cycle is a continuous one, but a certain amount of new power must, of course, be continually expended to

keep up the supply of compressed air, which is discarded as soon as it has taken up its quota of heat. Plants of this kind were once largely used; but, on account of their lack of efficiency, and the availability of better appliances, are now seldom seen.

The Simple Vacuum Machine.—Vacuum machines constitute a class of refrigerating apparatus in which water is the refrigerating agent. In simple form, the principle under which they operate is much like that of a compression machine. A vacuum pump is provided to exhaust the air from a closed chamber, in which a vessel containing the water to be frozen is placed. The lowered pressure brings down the boiling point of the liquid, a violent ebullition ensues, and the refrigerative effect produced by the vaporization of a part of the water turns the rest into ice. The latent heat of ice being 144, and that of steam at 32°F., 1,091; theoretically, the evaporation of 1 lb. of water should produce something over seven pounds of ice.

The latent heat of steam being great in comparison with the specific heat of water, the theoretical efficiency of a vacuum machine will be found to be much greater than that of any other machine of the compression type. This however is entirely offset by the tremendous size of the compressor required, which is 200 times as large as an ammonia machine to do the same work.

If the temperature wanted is lower than that of freezing water, brine must be placed in the freezing chamber instead of pure water, to prevent it from freezing and so stopping the operation.

Compound Vacuum Machine.—To make possible a vacuum machine of reasonable size, a process has been devised whereby the moisture evaporated from the freezing chamber is absorbed by some chemical agent, usually sulphuric acid, and the work on the air pump, in this way, much decreased, Of course, the concentrated acid which is used, soon takes up so much water that its efficiency is destroyed, when it must be re-concentrated by heating; and the fuel used to do this must be considered as part of the operating expense. Vacuum machines working on this principle are relatively small in size, but, if the operation is to be continuous, there must also be provided a pump to handle the dilute and also the reconcentrated acid, and some sort of exchanger to effect a transfer of heat from the strong acid leaving the reconcentrator, to the cold weak acid on its way from the absorber to the reconcentrator. One of the great disadvantages attending the use of sulphuric acid is the fact that all apparatus and piping with which the acid comes in contact must be lined with lead. This form of machine is rather troublesome to operate, but, for ordinary temperatures, its efficiency may be considered as fairly good.

Southby & Blyth Vacuum Machine.—A machine has been devised by these gentlemen, in England, which comprises the usual vacuum box, a large vacuum pump, a small splash air pump, and a water cooled condenser. In beginning operation, the small pump is used to remove the air from the refrigerating chamber, after which the larger pump is set to work to withdraw the water vapor, discharging the same into the condenser. In order to make this pump operative, so that the compressed vapors may be discharged without condensing in the pump, the pump cylinder is heated, and the small air pump is kept in operation to free the condenser from any occluded air which may come over with

the vapors. Owing to the fact that the piston pressure is less than one-fifth of a pound per square inch the compressor operates smoothly and with little friction. The apparatus is best adapted for use on a small scale in places where the use of ammonia or other noxious gases could not be risked.

Refrigeration by Liquefied Gases.—This method of refrigeration has no practical value from a commercial standpoint at the present time, on account of the great cost of producing refrigerants of this type. For the production, however, of extremely low temperatures, chiefly for medical purposes, or for physical, or chemical experiments, the use of liquefied air, and possibly other liquefied gases cannot be over-looked, or passed by without a brief exposition.

Many of the so-called permanent gases were liquefied on a small scale long ago by such scientists as Faraday, and later, on a larger scale, by Pictet and others, who used, not only pressure, but also a series of other liquefied gases, the first cooling the next, and so on, until finally a temperature obtained, low enough to liquefy the gas experimented with.

A few years ago, however, these costly laboratory methods, were superseded by a practical process devised by Professor Linde, who combined enormous pressures with a cumulative self-intensifying system of refrigeration, by which the liquefaction of air, nitrogen, oxygen, etc. can be produced on a large scale, at a slight expense.

The Linde Liquid Gas Process.—By this method, the gas to be liquefied is compressed by a powerful compressor, then sent through water cooling-coils to remove the heat of compression. From there it is forced through a coil several hundred feet long, which terminates in an expansion valve connecting with a liquid receiver. Leaving this receiver is another pipe, which concentrically surrounds the first pipe throughout its entire length, and then leads back to the suction side of the compressor.

The compressed gas, expanding into the liquid receiver, generates a certain amount of refrigeration, or, in other words, lowers its own temperature. Then, as it flows back to the compressor through the annular space between the concentric pipes, it absorbs a certain amount of heat from the gas in the central pipe, moving toward the liquid receiver, so that when the first gas reaches the compressor, ready to be compressed again, it has lost the exact equivalent of the B.t.u. removed from it on the first round in the water cooling-coils. It is then compressed again, and leaves the compressor and the water cooling-coils with the loss of another modicum of thermal units, so that when it reaches the receiver a second time, its temperature is lower than before, and its pressure higher.

So it goes round and round, on each trip exchanging heat with the gas in the other circuit of the pair of long concentric pipes, and at each passage through the water cooling-coils losing a certain number of thermal units, part of which are expressed in a lower temperature, and part in a higher pressure, until at last it reaches the critical point, and condenses into a liquid in the liquid receiver.

The process is continuous, so that when the liquid has once commenced to collect in the receiver, an additional amount is made with each stroke of the compressor. New gas to take the place of that liquefied, is continually supplied to the compressor at high pressure, from an auxiliary compressor and a second water cooling-coil. The entire apparatus, of course, must be heavily insulated, so that practically no exchange of heat can take place with the outside air or surrounding objects.

Practical Uses of Liquid Air.—The production of liquid air is probably the crowning achievement of the Linde gas-liquefying apparatus. Its availability

as a refrigerant for the production of extremely low temperatures for medical and experimental purposes has already been referred to. Among its other important uses are the following.

Liquid air can be used for the production of liquid oxygen, which is, in reality, when produced by the Linde process, a mixture of oxygen and nitrogen, consisting principally of oxygen. The process is based on the fact that when liquid air is vaporized under certain conditions, the nitrogen vaporizes first, leaving most of the oxygen behind. Linde devised a special apparatus for the manufacture of this so-called "Linde oxygen," which is a valuable agent in connection with certain manufactures.

Another valuable field for liquid air is the cheap and quick production of high vacua. The vessel to be put under vacuum is filled with some gas more easily liquefied than air, a neck being provided which is capable of being sealed off by the blow pipe. The neck is then immersed in liquid air, and when the gas has all condensed into it, it is isolated and removed, leaving a fine vacuum behind.

Expansion Side of Compression System.—The refrigerating medium, having been passed through the compressor, and condensed into a liquid by the condenser, is conducted to what is known as the liquid receiver, where it is stored up ready to be used when needed to produce cold, or, in other words, to absorb heat from the material which it is required to cool. In order to produce this refrigerating effect, the liquefied refrigerant must be released, through what is known as an expansion valve, into the interior of a system of pipes, coils, or other confined vessels, through the walls of which the heat of the surrounding liquid or air is absorbed by the refrigerant, as it vaporizes again to a gas.

The so-called expansion valve is a species of needle valve, arranged so that it may be opened very gradually, and so regulate with great nicety the amount of the refrigerant passing through it in any given time, and the cooling pipes or conduits, in the interior of which the refrigerant is allowed to vaporize again to a gas, are known as the expansion coils.

The temperature of the expanding refrigerant in these coils, and, as a consequence, the cooling effect which will be produced by it, will depend upon its pressure; and this may be regulated by opening or closing the expansion valve, or altering the speed of the compressor.

Cold Storage Rooms.—The simplest method of cooling any substance is to place it in a room which is under refrigeration, or, in other words, which is kept at a low temperature. The first requisite of a cold-storage room is that it must be well insulated, that is, constructed in such a manner that heat from the outside cannot readily penetrate into it through its walls, floor, or ceiling. This is accomplished by lining the room on all sides with what is known as insulating material, and the value of any such material is based on the number of B.t.u. which will pass through each square foot of it, per day of 24 hr. for each degree Fahrenheit by which the temperatures inside and outside may differ.

This number of B.t.u. is known as the coefficient n of the material in question. Below will be found a table giving the value of n for layers of various materials 1 ft. thick.

Confined air, in itself, is an excellent insulator, but it must be rigidly confined in small cells, and the whole kept perfectly dry. In fact, with most of the commonly used insulating materials, which are usually employed in small aggregates packed

tightly together, it is believed that the air confined in the interstices plays no small part in producing a high insulation. Moisture, on the other hand, is most injurious; and no insulation of any kind can be expected to remain efficacious, unless dampness is wholly excluded.

As a general proposition, it may be stated that a wall, ceiling, or floor, with first-class insulation, will pass from 1 to 2 B.t.u. per degree Fahrenheit difference, per square foot, per 24 hr.; while a good insulation will pass from 2 to 3 B.t.u.; and a poor insulation, 3 B.t.u. and over.

Among the insulating materials most used, a material known as cork-board stands pre-eminent. It is manfuactured out of natural cork, which is, for the most part,

VALUE OF INSULATING MATERIALS 1 FT. THICK

Material	Value of n in B.t.u.
Dry pine wood	2 0
Mineral wool	1 6
Granulated cork	1.3
Dry wood ashes	1.0
Dry sawdust	1 1
Dry powdered charcoal	1.3
Dry cotton	0 7
Dry soft paper felt	0 5

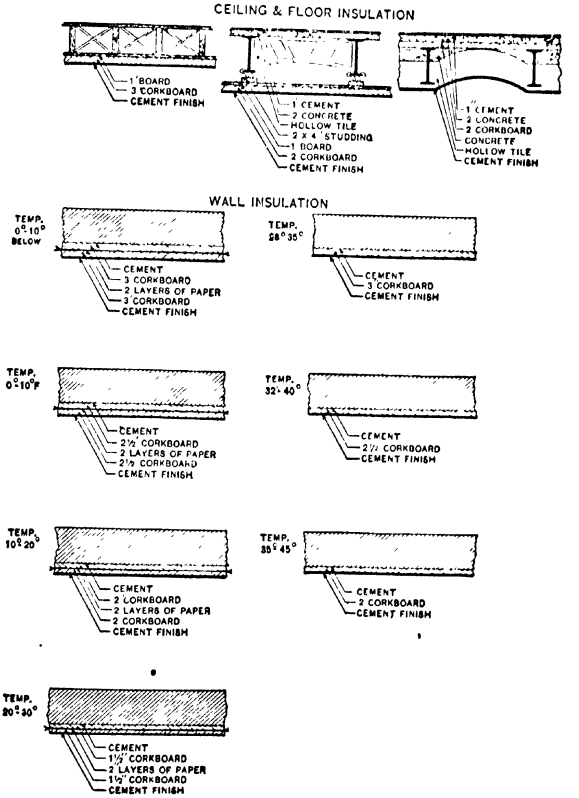


FIG. 5.—Cork-board construction.

imported from Spain. The cork is brought to this country in its natural condition, ground up into small fragments, and then dumped into a metal box and pressed tightly together by a powerful hydraulic press to form a thin slab, after which the slab, with the box still confining it, is run into a hot oven, where the natural gum in the cork is melted, and cements the whole together into a permanent sheet, from 2 to 4 in. in thickness, as a rule.

The finished material is usually to be had in slabs, approximately 3 ft. long, 2 ft. wide, and of any desired thickness, according to the work required of it. A sheet 2 in. thick will have a heat leakage value of 5 B.t.u., per square foot, per degree difference, per 24 hr. The walls of an ordinary ice box are usually lined with from 2 to 6 in. of cork-board, depending upon the temperature of the outside air, and the degree of cold to be maintained inside the box. A layer of cork-board 6 in. thick has a heat leakage factor of only 1.6 B.t.u. per square foot.

In Fig. 5 will be found some details of the usual method of insulating ceilings, walls, and floors with this material. For these refrigerated rooms, regular cold-storage doors are to be had upon the market. They are wooden doors, insulated with granulated cork, and built with a tapered or rabbetted edge, where the door proper meshes with the heavy framework. Their heat leakage factor is in the neighborhood of 2 B.t.u.

Cooling of Cold Storage Rooms.—The refrigeration of these cold-storage rooms is accomplished by means of pipe coils, hung up, either on the side walls or on the ceiling of the room, and the pipes themselves are cooled either by the liquid ammonia itself, expanded directly into the pipe, or by brine at a low temperature circulated through them by what is known as a brine pump.

The first of these methods of cooling the pipes is known as direct expansion, and the second, as brine circulation. Whichever system of cooling the pipes is employed however, the rate of heat transfer between the pipes and the still air of the room is 1.7 B.t.u. per square foot of outside pipe surface, per degree Fahrenheit difference between the temperature of the pipes and that of the room, per day of 24 hr. By grouping the cooling coils of such a room in a battery, and circulating the air of the room through them, by means of a fan, at a velocity of from 900 to 1,200 ft. per minute, this rate of heat transfer may be increased to 5, or even 6, B.t.u., as a maximum.

Practically, in order to obtain effective cooling without the installation of an excessive quantity of pipe, it is usual to assume that the temperature of the cooling medium in the inside of the pipe will be at least 20°F. lower than the temperature required for the air of the room, and all pipe surfaces are figured on that basis.

The Brine Cooler.—Where cold brine is to be used as the circulating medium, it is most efficiently cooled by means of a multi-pass, shell-and-tube type, brine cooler. A brine cooler of this type consists of a steel shell, cylindrical in form, with steel tube sheets near each end, into which a large number of longitudinal tubes are expanded. Cast-iron heads, with baffles or partitions forming an integral part of them, are fitted over the tube sheets at the ends of the cooler; and these are so designed as to cause the brine to pass successively through the tubes six or eight times before it finally leaves the cooler. In this way the brine is caused to pass through the tubes at a high velocity, resulting in a high rate of heat transfer between the ammonia and the brine, and this is further increased to a maximum by the presence of a liquid on each side of the tube walls.

Brine coolers are generally operated on the flooded system, or, in other words, an

excess of ammonia is continually fed into the brine cooler, so that it will absorb a maximum amount of heat from the brine passing through the cooler. The rate of heat transfer between the ammonia and the brine is, under these conditions, 80 B.t.u. per square foot of outside pipe surface, per degree Fahrenheit difference between the ammonia and the brine, per hour. The difference in temperature between the ammonia and the brine is generally figured at 10°F.; but for extreme conditions, as, for instance, where a low brine temperature is necessary, notwithstanding the fact that the back pressure on the compressor is high, by making the brine cooler very large this difference in temperature can be reduced to 5 or 6°F.

Throughout this entire section, the rate of heat transfer has been spoken of as being based on the degree of temperature difference existing on the two opposite sides of the cooling surface. In arriving, however, at this temperature difference, it should be borne in mind that it is the logarithmic mean temperature difference, and not the arithmetical mean temperature difference, which must be used. The reason for this is that when a warm body which is to be cooled, and the cooling medium which is to be heated, first come into contact with each other, the rate of heat transfer is greater than at the end of the cooling period when the temperatures are nearer together and for this reason the mean temperature follows a curve instead of a straight line.

Cooling of Liquids. Any liquid, of course, may be cooled in an appliance similar to the brine cooler already described, and such a cooler may be operated either on the flooded system or with closely regulated expansion valve, which will admit only sufficient ammonia to effect the desired amount of cooling. When so operated, however, the medium on one side of the tube walls will be ammonia gas, and the transfer of heat, under these conditions, will be 25 B.t.u. per square foot of outside tube surface, per degree Fahrenheit difference, per hour, in place of 80 B.t.u. with the flooded system.

Another common method of cooling a liquid is to cause the liquid to flow down by gravity over a vertical bank of coils, through the interior of which the refrigerating medium is circulated. With this method, extremely good results are possible, as the close contact existing between the surfaces of the pipes, and the thin layer of the liquid flowing over them at a relatively high velocity, causes a rate of heat transfer of at least 70 B.t.u. per square foot of outside pipe surface, per degree Fahrenheit of temperature difference, per hour.

Another method of cooling a liquid, which is much used in places where the danger of freezing and bursting the pipes can be ignored, is by passing it through a double-pipe cooler. This consists of two continuous concentric pipes or pipe circuits, usually built in the form of a flat coil like that already described and illustrated for the double-pipe ammonia condenser (see Fig. 2). The refrigerating medium is circulated through the inner of the two pipes, while the liquid to be cooled is made to flow through the annular space between the inner and outer pipes. As the area of the annular space is quite small, the liquid may be made to flow through it at a very high velocity, thereby greatly increasing the rate of heat transfer. With a speed of from 250 to 300 ft. per minute for the liquid to be cooled, a rate of heat transfer can often be attained as high as 125 B.t.u. per square foot per degree Fahrenheit difference, per hour.

Still another method of cooling a liquid is to place it in a brine-jacketed tank. This, however, is probably the least efficient method of all, on account of the usual lack of conductivity of the liquid itself. The efficiency of cooling tanks of this kind may be greatly increased if they are provided with moving paddles to keep the liquid in motion; but nothing like a maximum efficiency can be obtained, even in this way. This method is seldom used, except where it is desired to hold a large body of liquid under refrigeration while in storage.

In general, it may be said that cold-storage room piping should be figured on the basis of a 20°F. difference between the medium in the pipes and the desired temperature in the room; and, on this basis, 280 sq. ft. of external pipe surface per ton of refrigerating effect will be required. Where double-pipe brine coolers are used, there should be allowed approximately 15 sq. ft. of cooling surface per ton of refrigerating effect; and with shell- and- tube coolers, 10 sq. ft. per ton.

Ice Making.—The manufacture of artificial ice is carried on, for the most part, by one or two systems, which are known as the can system and the plate system. The can system is the one most generally used.

Can System.—A standard ice plant of this type consists of a steel tank, usually constructed of ¼ in. metal, strongly riveted together, and filled with brine, in which are placed cans filled with the water which is to be frozen into ice. Running longitudinally in the interior of the tank, along its sides and between each row of cans, below the surface of the bath of brine, are placed a succession of cooling coils, which keep the temperature of the brine down to between 15 and 18°F. The tank itself is heavily insulated, both sides and bottom, with several inches of cork-board, and its top is covered with a heavy wooden framework, with long rows of carefully fitted covers, 2 or 3 in. thick, one of which is just above the top of each can, so that it may be removed and the can lifted out when the water which it contains has been frozen into ice.

The ice cans are made of No. 16 galvanized iron, of a size to conform to the weight of the ice block which is to be manufactured. They are filled with water, and are then kept submerged in the cold brine until they are frozen solid. A standard commercial cake is supposed to weigh 300 lb., and the can designed to produce an ice block of this weight is 11½ by 22½ in. at the top, and 10½ by 21½ in. at the bottom, and 44 in. high. When it is immersed in a brine bath of from 15 to 18°F., it requires two full days to freeze it solid. This means that when a tank of this kind is designed to produce a given amount of ice per day, twice as many cans must be provided for as are needed for a single day's output.

Cooling Surface in Ice Tanks.—The cooling coils in the ice tank are operated by direct expansion or, in other words, they are fed direct with liquid ammonia through an expansion valve. In regard to the proper quantity of cooling surface to be installed in ice tanks, it is generally conceded that about 130 sq. ft. per ton of ice per day is the most efficient amount. The cooling coils are usually made of 1¼ in. pipe, and it requires 300 lin. ft. of this pipe to make up 130 sq. ft. of surface.

Hygienic Ice.—In making ice by the can system, the water to be frozen must be practically free from impurities. Even occluded air is objectionable, as it is almost sure to make the ice milky. Other impurities, such as earthy salts, metallic oxides, etc., produce unsightly streaks as the water is gradually frozen, beginning at the sides of the can, and finally concentrate in the center of the block, to form a dark-colored, and often evil-smelling, core.

The general practice, in the manufacture of the (so called) hygienic ice, is to freeze the ice from water obtained by condensing the steam exhausted from the steam engine which drives the plant. Water so obtained is free from earthy and metallic impurities, but must be re-boiled to remove all air, and subjected to an elaborate filtering, cleansing, and de-odorizing process to remove all traces of cylinder oil and make it sweet. All this adds to the cost of manufacture.

The greatest objection, however, to this plan is the fact that it limits the efficiency of the plant, for even with the most wasteful and uneconomical type of steam engine to drive the machinery, the exhaust steam is hardly enough to furnish the necessary condensed water from which to make the ice, and more must be furnished direct from the boiler.

Plate-ice Process.—The disadvantages of manufacturing ice by the ordinary can system, which requires that the water, to be frozen into ice, should be subjected to a preliminary treatment for the removal of its impurities, has led to the development of what is known as the plate system. In making ice by this method, the liquid refrigerant, or cold brine, is made to circulate through a system of flat coils clamped between iron plates. These are suspended in a tank filled with water, and the ice gradually forms on both sides of the plates, building itself up, little by little, into a solid cake of the desired thickness, and leaving behind the occluded air and the impurities which the water may contain.

With this process, no preliminary preparation whatever is required for the water which is to be frozen. But, on the other hand, a large degree of skill on the part of the operators must be had to carry it through successfully. The time needed to freeze a plate of ice 12 in. thick is about 7 days; and when the freezing is complete, the two huge sheets of ice, weighing many tons, must be detached from the plates by the aid of warm water, and sawed up into blocks of the desired size. The original ice sheets are usually about 12 by 20 ft. in area.

The advantage of this system, as has been stated, is the possibility of manufacturing clear and colorless ice from water which contains a large percentage of impurities. The disadvantages are the large first cost of the plant, the difficulties attending its successful operation, and the long time required to freeze a 12-in. cake, which is, of course, due to the fact that the freezing is done wholly from one side, and the last layer of ice on the outside must be frozen through nearly 12 in. of ice already in place. For these reasons, comparatively few plants of this type have been built.

Raw-water Ice Plants.—Some years ago, it was discovered that clear colorless ice could be frozen in cans, from natural water of reasonable purity, if, during the entire process of congelation, the water was continuously aërated and agitated by a stream of air bubbles passed up through it. A number of plants were built to operate on this principle, but always they failed from the same cause. An ice plug invariably formed in the air pipe, and stopped the process before the freezing was complete. Many plans were tried out, in the effort to obviate this difficulty, but without success; after a long series of experiments, conducted by the writer at the plant of the Baltimore Independent Ice Co., in 1912, a feasible scheme, was developed by which the continuity of the aërating process was made certain and accident proof, so that every cake of ice produced in a large tank could be depended upon to be clear and perfect.

By this method, a system of air headers is run along the top of the freezing tank, past each can, just underneath the wooden covers. The headers are supplied with compressed air at 20 lb. pressure and, through a series of air cocks, communicate with the interior of each ice can at the bottom, by means of a short, heavy, flexible rubber-pipe link, terminating in a metal drop pipe. Between the air cock and the flexible connection—and right here is the crux of the whole process—is a pin-hole orifice, through which the air must pass on its way to the can. So long as everything goes along normally, the tiny stream of air, forced through the pin-hole, passes on through

the rubber hose and drop pipe, and bubbles up through the can of water quietly; but let a plug of ice form to obstruct the flow of air, the pressure behind it will build up at once, until the ice is forced out of the drop pipe and normal conditions re-established. By this plan, a minimum of attention is required on the part of the attendants, quite a necessary condition, as it would be manifestly out of the question to have men lifting the covers from can after can, all day, to see if the air pipes were open. Every successful raw-water ice system in use today utilizes this pin-hole orifice, or a substantial modification of it.

The air for aerating the freezing water is furnished from an air compressor, and after being compressed is passed through a suitable cooler, which reduces its temperature approximately to that of the freezing tank and at the same time removes most of its moisture. By the use of this process, ice may be obtained which is clear and colorless throughout the whole cake, only a faint whitish trace marking where the air pipe passed down through the can. In some cases, however, where there are highly colored impurities, it is necessary, when the cake of ice is almost frozen, to remove the remaining contaminated water from the core, replacing it with some that is clean, in this way avoiding the presence of a dark-colored lump in one end of the cake.

The modern ice plant of today is necessarily of the raw-water type, as either of the two older processes is far too expensive in fuel. With the hygienic ice plants of 10 years ago, a production of six tons of ice, per ton of coal burned, was considered satisfactory. With the best class of raw-water plants now being built, the ratio is approximately twenty to one. Beyond this, what is more important, in these days of scarcity of help and other uncertain conditions, is the fact that raw-water plants require no steam boilers necessarily. So electric power may be used whenever it is available.

The Operation of Ammonia-compression Plants.—Since the efficiency of a refrigerating machine is proportional to the number of pounds of gas it handles, as expressed in cubic feet, in accordance with the particular conditions under which it operates, care should be taken that the suction gas, as it enters the compressor, has a temperature corresponding, as nearly as possible, to the suction pressure under which the machine is working. To ensure this condition, the expansion valve, which controls the flow of the liquid into the cooling coils, should be opened widely enough to permit the coils to fill themselves up with the refrigerant. This being done, the suction gas leaving the coils is not superheated above its proper temperature.

The presence or absence of superheat in the suction gas can best be determined by placing a thermometer in the main suction pipe, close to the machine. By closely watching this thermometer, and regulating the plant accordingly, a maximum of operating efficiency can be obtained; for not only will the compressor itself be working under the most economical conditions, but the cooling coils, completely filled with the liquid refrigerant, will present a pipe surface every square inch of which is thoroughly wetted. In no other way can maximum efficiency be obtained from cooling surfaces.

Miniature Ice Plants.—During the last few years, a number of small compact ice plants have been devised for use in private homes, small shops, or isolated places where a regular supply of commercial ice cannot be had. They are generally driven by some form of oil engine, or by electric motors, and have all parts of the "high" side integral on one base.

Figure 6 shows a plant of this type driven by an electric motor, a description of which will serve for them all. Externally, the assembled plant takes the form of an

electric motor and two cylindrical bodies, mounted side by side on an iron base. One of the cylinders contains the rotary gear-type compressor, with its iron housing, all being submerged in a bath of oil which fills the lower part of the cylinder. The compressed gas is discharged into the upper part of the same cylinder, above the oil,

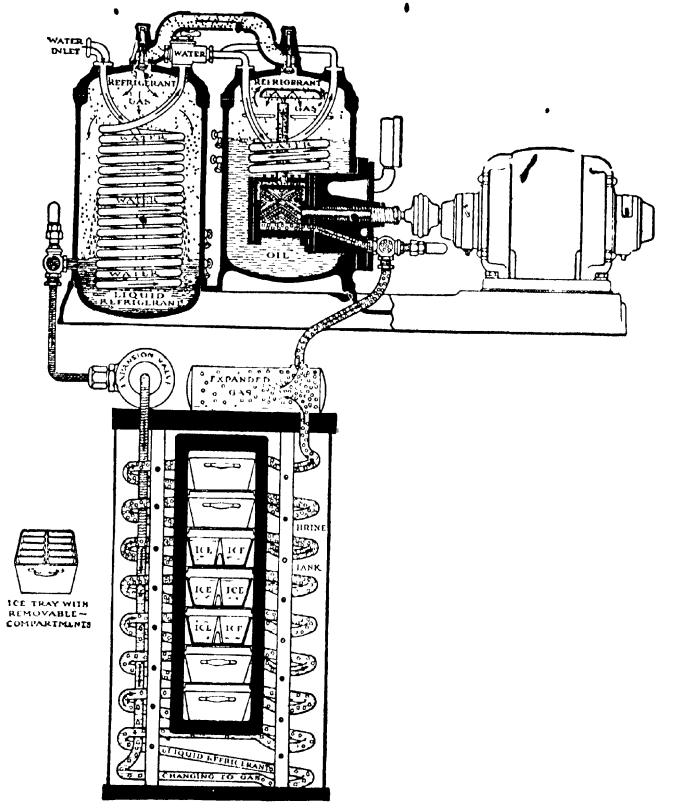


FIG. 6.—Miniature ice-plant.

and from there passes through a bent pipe to the top of the other cylinder, which is a combined condenser and liquid receiver.

The cooling water enters at the top of the second cylinder, and first passes through a helical coil, condensing the compressed gas into a liquid which collects in the bottom of the chamber. From there the water passes on to a second coil, submerged in the oil bath of the compressor cylinder, where it serves to cool the oil and, incidentally, the compressor immersed in it, after which it flows away to waste. The lubrication of the compressor is automatic, from the bath of oil with which it is surrounded, small pin-holes being provided at the proper locations for the passage of the lubricant.

The lower part of the illustration is the expansion side of plant. This consists of a tank filled with brine, in which are immersed the expansion coils, in which the refrigerant is expanded back to a gas. The liquid refrigerant is fed from the receiver in the

bottom part of the second cylinder, through an expansion valve, to these coils; and the expanded gas passes on to a small horizontal container, as shown, from which it is drawn out by the compressor, in this way completing the cycle. The brine tank is designed to be located in the interior of the ice box which the plant is supposed to serve, and the supply of brine contained in it acts as a reservoir of refrigeration, so to speak. A chamber is provided in the center of the brine tank designed to contain cans filled with water to be frozen into blocks of ice.

The Conditioning of Air.—Some years ago it was noticed that, by eliminating moisture from the air which is blown into a blast furnace, the quantity of coke required to melt the charge was materially reduced and a patent based on this idea was granted to James Gayley of the United States Steel Corporation. According to his process, the air was passed through a large chamber, filled with heat-absorbing pipes, through which either cold brine or liquid ammonia was fed. For this purpose brine is most generally used, and the temperature of the air is lowered to a point where its remaining moisture content is less than 1 gr. per cubic foot, after which the air is heated up again, before it is sent to the blast furnace.

With the exception of the work done in connection with the Gayley process, the art of air conditioning made very little progress until the beginning of the World War, when it was discovered that the use of conditioned air in certain processes connected with the manufacture of explosives had a great effect upon the time required for the complete burning of the powdered charge. For some time past, the U. S. Department of Agriculture has been making exhaustive studies on the effect of conditioned air in connection with the cold storage of food stuffs, etc., and it now looks as though, at no distant date, it might come to be one of the great uses of mechanical refrigeration.

From the standpoint of the amount of power consumed, the cooling of air is much more difficult than its heating. To heat air, it is simply necessary to supply enough B.t.u. to raise the volume in question a pre-determined number of degrees, and the heat required to raise the temperature of a given volume of air is relatively small, on account of the low specific heat of air.

When air is to be cooled, however, its moisture content must be taken into account, for in order to extract a pound of water from the air, it must be first condensed, and this requires a quantity of heat substantially equivalent to the latent heat of steam, or approximately 1050 B.t.u.

The process of cooling air, therefore, resolves itself into three parts: (1) The cooling of the air with its original load of moisture from the original temperature down to the temperature of saturation. (2) The condensation of sufficient moisture to produce the desired relative humidity at the pre-determined final temperature. (3) The cooling of the air with its remaining moisture content, and also the water which has been condensed out of it, from the point of saturation down to the final desired temperature, unless this water be previously drawn off.

In practice, the conditioning of air is usually carried on by first passing the air through refrigerated chambers, until its temperature has fallen to a point where its moisture content, in pounds at saturation, is equal to the number of pounds of moisture which will obtain at the desired ultimate temperature and relative humidity. All other moisture then condenses and is precipitated, after which the air, carrying only the proper amount of moisture, is heated to the required temperature by passing it over steam coils.

Below will be found a table giving the moisture content of air at various temperatures and percentages of saturation, by the aid of which any required calculations may be made.

POUNDS VAPOR IN 1,000 CU. FT. OF AIR AT DIFFERENT PERCENTAGES AND TEMPERATURES

Temperature, degrees Fahrenheit	Percentage saturation										
	50	55	60	65	70	75	80	85	90	95	100
100	1.411	1.552	1 694	1.835	1.976	2 117	2 259	2 400	2.541	2.682	2.823
95	1 223	1.345	1.467	1.589	1.712	1 844	1 977	2 089	2.201	2.323	2.446
90	1.056	1 161	1 267	1.373	1.479	1.584	1 690	1.795	1.901	2.005	2.110
85	0 909	1.000	1.091	1 182	1.273	1.364	1.455	1 546	1.637	1.728	1.819
80	0.781	0 859	0 937	1.015	1.093	1.166	1.249	1.327	1 405	1.483	1.562
75	0 668	0 735	0 802	0 868	0.935	1 002	1.069	1. 35	1.202	1.269	1.336
70	0.570	0 627	0.684	0 741	0.798	0 855	0.912	0 964	1.026	1.083	1.140
65	0.484	0 532	0 581	0.629	0.678	0 726	0 775	0 823	0.872	0 920	0.968
60	0 410	0.451	0 492	0 533	0.574	0 615	0 656	0 697	0 738	0.779	0.820
55	0.346	0 380	0 415	0.449	0 484	0 519	0 554	0.588	0 623	0 657	0 692
50	0.291	0 320	0 349	0 378	0 407	0 436	0 465	0.494	0 524	0.553	0.582
45	0 243	0 267	0 292	0 316	0 341	0 365	0 390	0 414	0 439	0.463	0.487
40	0.203	0.223	0 244	0 264	0 284	0 304	0 325	0 345	0 366	0.386	0.407

Let us assume that a 60 per cent saturation, at a temperature of 65°F. is required for a certain service. The moisture content under these conditions, as shown by the above table, is 0.581 lb. of vapor per 1,000 cu. ft. Let us now take the natural air, whatever it may be, and cool it to 50°F. at 100 per cent saturation. The moisture content, whatever it may have been previously, will, in this way, be reduced to 0.582 lb. of vapor per 1,000 cu. ft., and when we have heated this air again, from 50°F. to 65°F., the air conditioning problem will be met for this particular case.

In conditioning air commercially, its temperature, as it passes through the brine-cooled chambers to deposit its surplus moisture, and also its final temperature, when it has afterward been passed over steam coils, is automatically controlled by thermostatic regulation, so that air conditioning, as it is practiced today, is quite automatic as well as extremely simple.

NOTE.—In the conditioning of air a combination of chemical and physical means, or of chemical alone, may be adopted. That is, the air may be passed over calcium or magnesium chloride to remove some or all of its moisture In event such chemical means are adopted, chemical control of the process is necessary for its greatest economy, for some of the hydrates of deliquescent compounds give up their water much more readily than do others, that is, with a much smaller consumption of heat units, and the process should be run so as to attain that minimum. Even if an entirely chemical or an entirely physical (refrigeration) method be adopted, it should usually be a two-stage-process —EDITOR.

SECTION XX

OXIDATION AND REDUCTION*

By E. P. Schoch[1]

PART I

Origin of Terms.—Oxidation was first used to denote the combining of oxygen with other elements or with their compounds (*e.g.*, $S + O_2 = SO_2$, $2SO_2 + O_2 = 2\,SO_3$. Next came the extension of the term to such changes as the following:

$$2H_2S + O_2 = 2H_2O + S_2$$

on account of which the above definition was extended to: oxidation is the combining of oxygen with, or the abstraction of hydrogen from, other elements or their compounds.

It was recognized long ago that some elements can exist in more than two oxidation stages: thus, the sulphur in H_2S is in the lowest oxidation stage; that in free sulphur in the next higher stage; that in SO_2 in a still higher stage; and the sulphur in SO_3 in its highest oxidation stage. Since, furthermore, hydration (*e.g.* $SO_3 + H_2O = H_2SO_4$), and the neutralization of an acid by a base do not involve the action of free oxygen, either directly or indirectly, it soon became evident that an element may be a component of entirely different compounds and yet be in the same oxidation stage in all of them. Thus, the iron in $FeCl_2$ and in $FeSO_4$ is in the same oxidation stage because both can be obtained from FeO by reaction with HCl or with H_2SO_4 respectively, *i.e.* by means of changes which do not involve oxidation and hence do not change the oxidation stage of the iron from what it is in FeO. The same considerations show also that in $FeCl_3$ the iron is in a higher oxidation stage than in $FeCl_2$—because $FeCl_3$ can be derived from Fe_2O_3 by reaction with HCl, and Fe_2O_3 would evidently be obtained from FeO by oxidation.

Naturally, the term oxidation was then extended so as to include any changes of an element from a lower to a higher oxidation stage irrespective of the manner in which the change is actually brought about, and hence it is also applied to changes in which oxygen takes no part (*e.g.* $2\,FeCl_2 + Cl_2 = 2FeCl_3$).

With the last definition, oxidation will designate widely different changes in the chemical compounds of the elements affected. Hence, it is difficult—if not impossible—to define oxidation by referring directly to the changes in chemical composition produced thereby, and another means is commonly employed. This will be presented farther on.

Reduction was first used by metallurgists to denote the extraction of metals from their ores. The latter usually contain oxides of the metals to be extracted, and the reduction involves the abstraction of oxygen from these compounds: thus reduction is merely the reverse of oxidation, and that is its significance in chemistry today.

Oxidation of One Substance Involves Reduction of Another.—When a substance, *e.g.*, sulphur,—is oxidized by the oxygen furnished through the decom-

*In preparing this section the author has taken many of the tables from his "Introductory Course of Lessons and Exercises in Chemistry" and has drawn extensively from the presentation of this subject in the latter.

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position of another substance which yields free oxygen readily—*e.g.*, $KClO_3$—then it is evident that the latter is reduced, and that *the amount of oxidation of the former* (*i.e.*, *sulphur*) *is dependent upon the amount of reduction of the latter* (*i.e*, *chlorate*). This is necessarily always true—even when the *oxidation* consists of actions other than the direct transfer of oxygen.[1]

Oxidation-Reduction Reactions in Non-Aqueous Mixtures.—In non-aqueous mixtures, particularly those which react at high temperatures, the actions frequently consist of the simple transfer of oxygen, and such actions require no elaborate theory for their consideration. Thus the action of lead on fused KNO_3, which is used to prepare KNO_2, evidently is expressed by the equation:

$$Pb + KNO_3 = PbO + KNO_2$$

Similarly, the action of litharge upon metallic sulphides (*e.g.*, PbS) as it occurs in assaying, is easily understood from the equation

$$PbS + 2PbO = 3Pb + SO_2$$

In more complex examples, we avail ourselves of the fact that many ternary compounds containing oxygen are numerically equal to the sum of two oxides which can exist separately. Thus Na_2SO_4 is numerically equal to $Na_2O.SO_3$. Formulas written thus are called "dualistic" formulas: they serve to show the relations between the oxidizer and the reducer in complex reactions in non-aqueous mixtures. Thus, when in the fusion of $MnO + K_2CO_3 + KNO_3$, the green manganate K_2MnO_4 is produced at the expense of oxygen from KNO_3, the relations are easily obtained from the following dualistic formulas of these substances:

KNO_3 written dualistically is $K_2O.N_2O_5$
K_2CO_3 written dualistically is $K_2O.CO_2$
K_2MnO_4 written dualistically is $K_2O.MnO_3$

N_2O_5 gives up oxygen and leaves 2NO which escapes as a gas. MnO takes up oxygen and becomes MnO_3. Hence, $2N_2O_5$ furnish enough oxygen for 3MnO. Since $3MnO_3$ combine with $3K_2O$, one molecule of K_2CO_3 will be required to furnish K_2O, while its CO_2 will escape as a gas. Hence the equation is

$$2(K_2O.N_2O_5) + 3MnO + K_2O.CO_2 = 3(K_2O.MnO_3) + 4NO + CO_2$$

Another example of the value of writing formulas *dualistically* is the following: potassium cyanate (KCNO) is made from potassium cyanide (KCN) by heating the latter with $K_2Cr_2O_7$. The oxygen is obtained from a part of the chromic acid oxide in $K_2Cr_2O_7$ ($K_2O.2CrO_3$). The K_2O retains one CrO_3, and the other is reduced to the form Cr_2O_3. These relations are satisfactorily expressed by the following equation:

$$3KCN + 2(K_2O.2CrO_3) = 3KCNO + 2(K_2O.CrO_3) + Cr_2O_3$$

For convenient reference, the dualistic formulas of some common substances are given here: sodium carbonate, $Na_2O.CO_2$; sodium silicate, $Na_2O.SiO_2$; sodium sulphate, $Na_2O.SO_3$; sodium sulphite, $Na_2O.SO_2$; sodium nitrate, $Na_2O.N_2O_5$; sodium nitrite, $Na_2O.N_2O_3$; calcium phosphate, $3CaO.P_2O_5$; chromium sulphate, $Cr_2O_3.3SO_3$; potassium chromate, $K_2O.CrO_3$; potassium dichromate, $K_2O.2CrO_3$;

[1] Logical procedure requires that *free oxygen be considered as being in the oxidized state*, and *combined oxygen as being in the reduced state*, so that the change of oxygen from the free element to any compound amounts to its reduction. Similarly, free hydrogen must be considered as being in the reduced state and combined hydrogen as being in the oxidized state. Thus the union of oxygen with hydrogen appears as the *reduction of the oxygen* and *the oxidation of the hydrogen*.

ferrous sulphate, $FeO.SO_3$; ferric sulphate, $Fe_2O_3.3SO_3$; manganous sulphate, $MnO.SO_3$; potassium manganate, $K_2O.MnO_3$; calcium permangante, $CaO.Mn_2O_7$; potassium chlorate, $K_2O.Cl_2O_5$; potassium perchlorate, $K_2O.Cl_2O_7$.

Reactions in Aqueous Mixtures.—The above procedure is quite satisfactory for reactions in non-aqueous solutions, but it is not satisfactory for reactions in aqueous solutions because in many of them oxygen is not transferred directly from the oxidizer to the reducer, or does not appear to take any part whatever. Hence, a more generally applicable theory is here to be introduced. It is applicable to all oxidation-reduction reactions without exception, and it represents the experimental facts directly—that is, it does not require the assumption of any hypothetical intermediate steps.

Valence Changes Due to the Liberation of Electrons Indicate Oxidation or Reduction.—It is desirable to have a simple means for recognizing oxidation changes Such a means should be something that is physically measurable, and applicable to all changes. For the treatment to be presented here we obtain a general indicator by considering the changes at the anodes of electrolytic or of battery cells, and this will be shown in the following examples.

Example 1.—In the electrolytic refining of silver, the silver anode dissolves in a nitrate electrolyte and forms silver ion (Ag^+), which together with the nitrate ion present corresponds to silver nitrate. This change from metal to a constituent of of this solution corresponds to the oxidation of the silver, because the same change could be accomplished through the following steps:

$$4Ag + O_2 = 2Ag_2O$$
$$Ag_2O + 2HNO_3 = 2AgNO_3 + H_2O$$

Since the second step does not change the oxidation stages of the elements involved, it follows that the first step—oxidation—is essential to the whole change. Hence, the same change in the state of silver, however produced, involves oxidation, and the anodic dissolution of silver considered in this example must involve oxidation.

The change at the silver anode is accompanied by the flowing of negative electric charges from the anode through the connecting wire to the remainder of the circuit. The amount of these electric charges is one faraday per 1-g. atom of silver, which corresponds to one electron (symbol, $\ominus$) per Ag.[1] Hence the equation for this change is:

$$Ag^\circ = Ag^+ + 1\ominus$$

This means that an atom of silver metal forms a univalent silver ion and one free electron.

From this example, we may formulate the following definition of oxidation: *Oxidation is a change in the valence of an element produced by its giving up electrons.*

Example 2.—When a solution of a chloride (*e.g.* HCl) is electrolyzed with a graphite or a platinum anode, the change at the anode consists of the discharge of chloride ions which produces free chlorine and free electrons according to the equation—

$$2Cl^- = Cl_2^\circ + 2\ominus$$

the free electrons constitute the electric current flowing from the anode through the connecting wires to the rest of the circuit.

[1] The electron is the *unit* charge of negative electricity: it is the amount corresponding to one negative valence and the amount required to neutralize one positive valence.

The above change in the state of the chlorine—from the compound HCl to free chlorine—can be brought about by direct oxidation, as in the Deacon process:

$$4HCl + O_2 = 2H_2O + 2Cl_2$$

Hence any other procedure for changing chloride ion to free chlorine is considered to be oxidation, and the anodic change above must involve oxidation.

The symbol for the chloride ion is Cl^- and for the electrically neutral element is Cl_2°. These symbols indicate that the change undergone by chloride ion at the anode amounts to the giving up of negative electric charges (electrons) as expressed by the equation:

$$2Cl^- = Cl_2^\circ + 2\ominus$$

From this we derive the same definition for oxidation as before: it is a change in the valence of an element produced by its giving up electrons.

The changes at the cathodes of electrolytic cells consist of the reverse of the changes at the anodes—and hence they are *reductions*. In these actions elements in various forms of combination combine with the free electrons coming over the wire to the cathode. Thus, in a cell with a silver salt solution for an electrolyte, the silver ions at the cathode combine with the free electrons coming to the cathode through the connecting wire, and form silver metal—according to the equation

$$Ag^+ + 1\ominus = Ag^\circ$$

The silver atoms form a deposit on the cathode surface.

Again, with an electrolyte containing free chlorine in solution, the cathode change consists of the formation of chloride ions, according to the equation

$$Cl_2^\circ + 2\ominus = 2Cl^-$$

The free charges for this change come through the connecting wire to the cathode.

Identity of Battery-cell Changes and Oxidation-Reduction Reactions.—A battery cell differs from an electrolytic cell only in the fact that the poles of a battery cell are composed of materials which, collectively, have a tendency to react so as to *send* electrons out from the anode through the connecting wire to the rest of the circuit, and when the battery is in action the current is allowed to flow in accordance with the battery's impulse; while the poles of an electrolytic cell are composed of materials which usually have no *tendency* to react in any sense, and in any case are impelled to change by an external force which draws the electrons out at a predetermined anode through the connecting wire. Otherwise there is no essential difference between these two classes of cells and all that has been said concerning electrolytic cells holds also for battery cells, that is, while the current flows, oxidation takes place at the anode and reduction at the cathode.[1]

Attention is now to be called to the following fact: *the sum total of the changes in a battery cell is an oxidation reduction reaction, and every mixture in which an oxidation-reduction reaction takes place contains also the essential elements for constructing a battery cell.*

[1] In assigning algebraic signs to cells, we must consider whether we are interested in the current *going in* or *coming out*. With electrolytic cells, we are interested in the current *sent in*—hence the pole at which we send the (*positive*) current in is designated as the positive pole, or the pole at which the (*negative*) electrons are sent in is called the negative pole. But with battery cells, we are interested in the current *coming out:* hence, the poles at which the (*positive*) current comes out is called the positive pole, or where the electrons come out is called the negative pole.

To demonstrate the truth of the above statement, let us consider the gravity or the Daniell cell, the negative pole of which consists of zinc dipping into zinc-sulphate solution, while the positive pole consists of copper surrounded by a saturated solution of copper sulphate. Different means are employed to prevent the two pole solutions from mixing mechanically—in the gravity cell, the positive copper pole with its heavy solution is placed in the lower part of the jar, with the negative zinc in the upper part and the lighter electrolyte of the latter floating on top of the copper sulphate solution. In the Daniell cell, one pole and its solution is placed in a porous earthenware cup which is placed in a larger glass container, and the negative with its solution is placed in the space between the glass jar and the porous cup.

When the poles are connected through a metallic connector, the cell will send the (positive) current from the copper pole (positive) through the wires to the other pole; or the electrons from the zinc pole (negative) through the wires to the other pole. The chemical change at the zinc pole consists of the dissolution of zinc, and is expressed by the equation:

$$Zn^{\circ} = Zn^{++} + 2\ominus$$

By definition, this change is oxidation: the zinc is oxidized. The change at the copper pole consists of the deposition of copper on the pole, and is expressed by the equation:

$$Cu^{++} + 2\ominus = Cu^{\circ}$$

By definition, this change is reduction: the copper ion is reduced. Furthermore, it is evident that the rate at which the copper is deposited depends upon the rate at which the electrons are supplied by the change of the zinc at the other pole, or in other words, when estimated in number of electrons, *the amount of oxidation taking place in any period of time is equal to the amount of reduction produced in the same time.*

The total change in the cell is the sum of the above two pole changes. Adding them algebraically, and simplifying by dropping the electrons from both sides of the equation, we obtain:

$$Zn^{\circ} + Cu^{++} = Cu^{\circ} + Zn^{++}$$

The accompanying anion requires a little consideration at this point. Since under equilibrium conditions, every portion of a solution contains equivalent amounts of cation and anion, the discharge of the copper ion at the positive pole will leave the liquid next to the pole momentarily with an excess of anion over cation. At the zinc pole the formation of zinc ion will leave the liquid next to that pole momentarily with an excess of cation over anion. This electrically unbalanced condition at the poles causes a slight shift of all the cations *toward*, and of all the anions *away from*, the zinc pole to an extent sufficient to "balance up" the excess of cations at the zinc pole and of anions at the copper pole (electric transfer of ions). As a result of this, the new zinc ions at the zinc pole are furnished sulphate ions in amount equal to those given up by the copper ions discharged at the copper pole.

Hence, we may add these "inactive" sulphate ions to our equation above, and this completes it to the usual form:

$$Zn^{\circ} + (Cu^{++} + SO_4^{--}) = (Zn^{++} + SO_4^{--}) + Cu^{\circ}$$

The foregoing chemical action in the battery cell takes place also whenever metallic zinc is dipped into a solution of copper sulphate. A vessel containing such a mixture really contains all of the essential elements of the above battery cell and wire connection, as may be seen by imagining the two metal poles brought together until they merge into one, and the connecting wire attains zero length, while the two liquids are

thoroughly mixed. Since the copper metal and the zinc sulphate are merely results of the actions, they need not be used to begin with, hence a rod of zinc dipped into copper sulphate solution contains all the essential parts of the "condensed" battery cell.

There is no reason why we should assume that the materials in this mixture should react in a manner different from the manner in which they react in the battery cell, hence the details of the action presented by the battery cell shows the details of the action in this mixture, and thus the battery cell enabled us to study oxidation-reduction actions much more in detail than we could otherwise.

It is evident that we can reverse the above process, namely, take the constituents of the oxidation-reduction mixture, and construct a battery cell: for this purpose we place the substance to be oxidized (*i.e.* zinc) at one pole, and the substance to be reduced (*i.e.* copper ion) at the other. To complete the mechanical arrangement, we must put a salt solution around the zinc, any salt solution will do provided it does not produce any change when these two are put together apart from the rest. For the copper sulphate solution, the completion of the pole evidently requires the supplying of an electric conductor—and this may be chosen at random from substances which do not change when these two are put together apart from the rest. Graphite, platinum, copper, etc., will evidently do for this purpose.

Since every mixture undergoing an oxidation-reduction reaction can generally supply the oxidizer and the reducer separately, and since each one of these can be supplied with such extra (inactive) parts necessary to complete the poles as shown above, it follows that every oxidation-reduction reaction can be studied as a battery cell.

Oxidation-reduction Reactions are Mostly Reversible.—If an outer electromotive force with a voltage greater than that of the above battery is applied to its poles in such a manner as to send a current in the direction opposite to that considered above, then the actions at the poles will, in most cases, take place in exactly the reverse sense: that is, the products of the above reactions will change back exactly to the original substances, as shown by these equations:

$$Zn^{++} + 2\ominus = Zn^{\circ}$$
$$Cu^{\circ} = Cu^{++} + 2\ominus$$

This perfect reversibility is true of most oxidation-reduction reactions.

Independence of Kind of Action at Poles of Battery Cell.—The kind of an action which an oxidizer (or a reducer) undergoes, and the force with which it tends to undergo this action are not in any manner affected by, or dependent, upon, the reducer (or the oxidizer) with which it is "coupled" in a particular mixture or battery cell. Thus the zinc pole used above may be coupled with a "silver nitrate-silver" pole in place of the "copper sulphate-copper" pole used above, and it will be found that the change at the zinc pole is then in no wise different from what it was before.

Measurement of Oxidizing Tendency.—If a voltmeter is applied to the poles of the Daniell cell above, it will register 1.1 volts. If a "silver nitrate-silver" pole is used in place of the copper pole, the cell will exert 1.56 volts. A chlorine pole may be made up of a solution of chlorine in hydrochloric acid, with a rod of graphite dipped into the solution to make the electrical connection. When this is coupled with the zinc pole, and the voltmeter is applied to this cell, it will register 2.11 volts. The largest voltage with this zine anode would be obtained

if a fluorine pole could be coupled with it: the voltmeter would then register 2.66 volts.[1] The question arises: how much of these voltages is due to the zinc pole in each case? We do not know how much, but if, as stated in the preceding paragraph, the action of the zinc pole is not affected by the action in the other pole, then it exerts the same amount of electromotive force in each case.

In order to formulate a definite notion concerning the origin of electric charges (electrons) from different substances, we assume in accordance with the present day view of electricity, that metals differ in their tendencies to dissociate into free electrons and positive ions.[2] Since such resulting ions also react with electrons in the reverse sense, it follows that there must be an equilibrium between these two oppositely reacting substances—*e.g.*

$$Zn \rightleftharpoons Zn^{++} + 2\ominus$$

in the maintainance of which equilibrium each active component must be present in a certain concentration or exerting a certain "pressure." This must be true of the electrons as well as of the other components. Hence each single pole, when at equilibrium—*e.g.* when no current is passing through it—exhibits a particular *electron* pressure characteristic of its essential chemical ingredients. The two different poles of a cell exert different electron pressures, and when the wire circuit between them is closed, the electrons will flow from the pole of greater pressure through the wire to the pole of lesser pressure: hence the pole exerting naturally a greater electron pressure will have its substances reacting in such a sense as to replace the electrons sent out, while the other pole *must* react so as to use up the electrons received or "forced in" upon it.

The difference between the electron pressures of the two poles at equilibrium is commonly measured in volts.

Tabulation of Single Poles in Order of Forces.—In order to connect the voltages of all the electromotively active substances, we proceed as follows:

Since the above theoretical zinc-fluoride cell shows the largest voltage of any cell made up with this zinc anode, the fluoride cathode evidently exerts a lesser opposing voltage than any other cathode that could be connected with this zinc anode, and we may assume the voltage of the fluoride pole to be any small value—say 0.1 volts.[3] Then we have—"voltage of zinc pole *minus* 0.1 equals 2.66," or "force of zinc pole = 2.76 volts."

With this value for the zinc pole, the voltages of the other poles may be obtained from the cell measurements above by the following simple calculation, because, as pointed out above, the electromotive force of each pole is the same in all combinations.

[1] This value is obtained by calculation from other data, because a fluorine pole is experimentally impossible on account of the fact that fluorine acts upon water according to the equation.

$$2F_2 + 2H_2O = 2H_2F_2 + O_2$$

[2] Or, generally speaking, all valence changing atoms differ in their tendencies to dissociate into electrons and atoms charged less negatively to an extent corresponding to the number of electrons given up

[3] This value has been selected in order to make the voltage of the hydrogen electrode (No. 17 in the accompanying Table, p. 690) exactly 2 volts.

OXIDATION CHANGES ARRANGED IN DESCENDING ORDER OF THE ELECTRIC PRESSURES PRODUCED THROUGH THEIR REACTION TENDENCIES

Elements in reduced state (in order of decreasing powers of acting as reducing agents)	Relation of tendency to change from left to right expressed in volts	Elements in oxidized state (in order of increasing powers of acting as oxidizing agents)
1. Potassium metal	5 20	K^+ salt solution + 1⊖
2. Sodium metal	4 80	Na^+ salt solution + 1⊖
3. Calcium metal	4 50	Ca^{++} salt solution + 2⊖
4. Magnesium metal	3 50	Mg^{++} salt solution + 2⊖
5. Aluminum metal	3 00	Al^{+++} salt solution + 3⊖
6. Hydrogen gas	2 80	H^+ ion in NaOH solution (normal in OH^-) + 1⊖
7. Zinc metal	2 76	Zn^{++} salt solution + 2⊖
8. Sulphide ion (sodium sulphide solution normal in S⁻⁻)	2 55	S° element + 2⊖
9. Iron metal	2 43	Fe^{++} salt solution + 2⊖
10. Cadmium metal	2.40	Cd^{++} salt solution + 2⊖
11. Sulphide ion (saturated solution of hydrogen sulphide in pure water)	½ 35	S° element + 2⊖
12. Lead metal	2 34	Pb^{++} in dil H_2SO_4 + 2 ⊖ (saturated solution of $PbSO_4$)
13. Nickel metal	2.17	Ni^{++} salt solution + 2⊖
14. Sulphide ion (saturated solution of H_2S in normal HCl)	2 15	S° element + 2⊖
15. Lead metal	2 12	Pb^{++} salt solution + 2⊖ (normal in Pb^{++})
16. Tin metal	2 10	Sn^{++} salt solution + 2⊖
17. Hydrogen gas	2 00	H^+ ion in acids + 1⊖ (normal solution of H^+ ion)
18. Bismuth metal (same for Sb)	1 80	Bi^{+++} salt solution + 3⊖
19. Stannous ion (stannous chloride solution)	1 76	Sn^{++++} salt solution + 2⊖ (stannic chloride solution)
20. Mercury metal	1 72	Hg^+ salt solution + 1⊖ (Hg_2Cl_2 in normal Cl^- solution)
21. Copper metal	1.66	Cu^{++} salt solution + 2⊖
22. Iodide ion (normal in I^-)	1 46	I° element + 1⊖ (saturated solution of iodine)
23. Ferrous ion (solution normal in Fe^{++})	1 25	Fe^{+++} salt solution + 1⊖ (normal in Fe^{+++})
24. Silver metal	1 20	Ag^+ salt solution + 1⊖
25. Mercury metal	1 20	Hg^+ salt solution + 1⊖
26. Oxygen ion (in neutral solution)	1 18	Oxygen gas ($O°_2$) (saturated solution) + 2⊖
27. Bromide ion (solution normal in Br^-)	0 92	Br° element (saturated solution) + 1⊖
28. Sulphur in compounds, with valence less than 6 (+)	0 80	S^{++++++} compounds + free ⊖ (concentrated H_2SO_4)
29. Nitrogen compounds, with valence less than 5+	1 00 to 0 72	Compounds of NO_3^- ion + free ⊖ plus H^+ (HNO_3)
30. Cr^{3+} compounds	0 70	Cr^{6+} compounds + free ⊖ + H^+ (solution of chromic acid)
31. Chloride ion (solution normal in Cl^- ion)	0 65	Cl° element (saturated solution) + 1⊖
32. Mn^{++} compounds	0.48	Mn^{7+} compounds + free ⊖ + H^+ (solution of permanganic acid)
33. Cl° element	0 40	Cl in compounds where it has positive valences + free ⊖ + H^+ ($HClO$, $HClO_3$)
34. Oxygen ions (in any acid solution having very few O^{--} ions)	0 30	Oxygen gas liberated from a platinum pole by electrolysis of solutions of oxy-acids such as nitrates, sulphates, phosphates + free ⊖
35. Pb^{++} ion (in saturated solution of $PbSO_4$ in diluted H_2SO_4)	0 34	Pb^{++++} (from solid PbO_2 in diluted H_2SO_4) + free ⊖
36. Fluoride ion solution	) 10	F° element + 1⊖
37. Theoretical 0 pole	0 00	Theoretical 0 pole

(*a*) Force of zinc pole *minus* force of copper pole = 1 1 volts, or 2 76 volts − force of copper pole = 1.1 volts; hence, force of copper pole = 2 76 − 1.1 = 1.66 volts.

(*b*) Force zinc pole *minus* force of silver pole = 1.56 volts; or 2.76 volts − force of silver pole = 1.56 volts; hence, force of silver pole = 2 76 − 1 56 = 1 2 volts.

(*c*) Force of zinc pole *minus* force of chloride pole = 2 11 volts; or 2 76 volts − force of chloride pole = 2.11 volts; hence, force of chloride pole = 2 76 − 2.11 = 0 65 volts.

In the accompanying table, these forces of the single poles are tabulated in descending order of their values.

Oxidation Changes.—For the changes shown in the accompanying table all equations in the table were written so as to show the formation of free electrons—that is, in each example the material on the left side is in the *lower* oxidation stage, and on the right side in the *higher* oxidation stage: they all appear as oxidation changes.

The voltages in this table have been obtained by using poles in which all solutions have normal concentrations of the ingredients mentioned except where other concentrations are stated specifically in the table. Since the reacting tendencies of substances vary with their concentrations, it follows that the tendencies to reaction will be different when the concentrations of the substances are different from those given here: the voltages in the central column will be larger if the substances in the left column are employed in a more concentrated form than that here mentioned, the voltages will be less if the substances on the right are present in a more concentrated form than that here mentioned.

The relative tendencies to reaction indicated by the position of these substances in the table is not changed extensively by ordinary diluting or concentrating of the solutions; but with large differences in concentrations, such as the difference between the hydrogen ion concentration in an acid on one hand and in pure water on the other (the latter contains one-ten millionth as much H ion as the former[1]), the voltage of the same material has largely different values. Only on this account do some materials appear at several different places in the table. Compare No. 6 with No. 17, and No. 8 with 11 and 14.

In order that a particular reducer and a particular oxidizer may actually react when mixed, their positions in the table must have the following diagrammatic relation:

DIAGRAMMATIC RELATION (IN TABLE) OF REDUCERS TO OXIDIZERS WHICH ACTUALLY REACT ON MIXING

Reducer (chosen from left side)	changes to →	Products on same line	while oxidizer below reducer ↓
Products on same line	← changes to	Oxidizer (chosen from right side)	

This diagram should be "read" as expressing the following: the "reducer," found in the left-hand column, changes to the right to products on the same line, while an "oxidizer" found *below* these products changes to the left to products on the same line with it.

A reaction between a reducer and an oxidizer the potentials of which are close together does not continue until one or the other of these substances is exhausted because the lessening of the original materials brings the potentials closer together. Thus, a mixture of KI and $FeCl_3$ reacts as follows:

KI reacts thus: $2K^+I^- = I^\circ_2 + 2K^+ + 2\ominus$
$FeCl_3$ reacts thus: $2\ Fe^{+++}Cl_3^- + 2\ominus = 2\ Fe^{++}Cl_2^- + 2Cl^-$
Together, thus: $2KI + 2FeCl_3 = I^\circ_2 + 2KCl + 2FeCl_2$

With N/1 (I^-) solution saturated with I°_2, the potential of the first reaction is 1.46 volts and with a solution normal in both Fe^{++} and Fe^{+++}, the potential of the second reaction is 1.25 volts. Hence, with these concentrations, their combined action is impelled by 1.46 − 1.25 = 0.21 volts. But as the iodide is used up, the first potential becomes less, and as the Fe^{+++} is used up, the second potential becomes greater, so that they will finally become equal. Then their combined reaction has no voltage to impel it, and it ceases.

It is evident that with still smaller concentrations of iodide and Fe^{+++} the potentials will even have the reverse relations, and such a mixture will react in the opposite sense, *i.e.* so as to *produce* iodide and Fe^{+++} from I°_2 and Fe^{++}. This reversal of potential relations with simple changes in concentrations will occur in all cases in

which the potentials are close together, *e.g.*, with silver metal and mercurous salt (Nos. 24 and 25); copper and iodine (Nos. 21 and 22); etc.

Selection of Materials for Battery Cells or Oxidation-reduction Mixtures.—To select the materials for any battery cell possible with the common substances, proceed as follows. For the negative pole select any substance in the left-hand column of the table on p. 690, it will change to the corresponding substance in the right-hand column if any substance in the right-hand column on a lower line is placed at the positive pole or if these substances are put directly together. The second substance is forced to change to its corresponding substance in the left-hand column (on the same line!) because the change of the first substance produces a greater electron pressure than the second can withstand. The voltage of the cell is equal to the voltage of the first change minus the voltage of the second change.

The Daniell cell is made up by placing zinc (*i.e.*, No. 7 *left*) at the negative pole, and copper sulphate (*i.e.*, No. 21 *right*) at the positive pole. Its voltage is 2.66 − 1.56 = 1.10 volts. The reactions which take place are

$$Zn^{\circ} = Zn^{++} + 2\ominus$$
$$Cu^{++} + 2\ominus = Cu^{\circ}$$

Adding we obtain

$$Zn^{\circ} + Cu^{++} = Zn^{++} + Cu^{\circ}$$

To obtain the usual form, we add the "inactive" anions thus

$$Zn^{\circ} + (Cu^{++} + SO_4^{--}) = (Zn^{++} + SO_4^{--}) + Cu^{\circ}$$

Other cells in which the same kinds of changes take place—of a free metal at the negative pole and of a metal ion at the positive pole—are easily made up from the table in the same way.

Another well known kind of oxidation-reduction reaction—namely the displacement of bromine or iodine by chlorine—is obtained by coupling No. 22 *left* with No. 31 *right*. The reactions which take place are

$$2I^{-} = I^{\circ}_2 + 2\ominus$$
$$Cl^{\circ}_2 + 2\ominus = 2Cl^{-}$$

Adding we obtain:

$$2I^{-} + Cl^{\circ}_2 = I^{\circ}_2 + 2Cl^{-}$$

To obtain the usual form of the equation, we must add the inactive cation—

$$(2K^{+} + 2I^{-}) + Cl^{\circ}_2 = (2K^{+} + 2Cl^{-}) + I^{\circ}_2$$

A third kind of oxidation-reduction reaction is obtained by coupling No. 19 *left* with No. 23 *right:* since the total number of electrons formed by the oxidized substance must be taken up by the reduced substance, the equation for No. 23 must be multiplied by *two* throughout. Thus we obtain:

$$Sn^{++} = Sn^{4+} + 2\ominus$$
$$2Fe^{+++} + 2\ominus = 2\ Fe^{++}$$

Adding and inserting the inactive anions present, we obtain:

$$SnCl_2 + 2FeCl_3 = SnCl_4 + 2FeCl_2$$

Any other oxidation-reduction reaction that will actually take place may thus be ascertained from the table, and the equation derived as shown here.

Special properties and other data concerning the substances which take part in oxidation-reduction reactions are given below under sections devoted to the different

elements. However, before proceeding to those sections, we must consider the single reactions of ternary and other polyatomic oxidizing (or reducing) agents.

Calculation of Polar Valences of Atoms in Compounds of More than Two Different Elements.—In oxidation-reduction actions, many ternary compounds—such as HNO_3—or ions composed of radicals—such as NO_3^-, undergo changes which indicate that they can ionize in a manner different from the ordinary. Thus the fact that NO_2, HNO_2, NO, N_2O, or N_2 may be obtained from HNO_3 by different reducing actions indicates that the latter may form any one of the following sets of products:

(*a*) H^+, O^{--} and NO_2;
(*b*) O^{--} and HNO_2;
(*c*) H^+, $2O^{--}$ and NO;
(*d*) $2H^+$, $5O^{--}$ and N_2O (from $2HNO_3$);
(*e*) $2H^+$, $6O^{--}$ and N_2 (from $2HNO_3$);

All of these sets of products have an excess of negative charges over positive charges, and since HNO_3 *as a whole* is electrically neutral, it follows that this excess of negative charges must have been added from without—as expressed by the following equations:

(*a*) $HNO_3 + 1\ominus = H^+ + O^{--} + NO_2$
(*b*) $HNO_3 + 2\ominus = O^{--} + HNO_2$
(*c*) $HNO_3 + 3\ominus = H^+ + 2O^{--} + NO$
(*d*) $2HNO_3 + 8\ominus = 2H^+ + 5O^{--} + N_2O$
(*e*) $2HNO_3 + 10\ominus = 2H^+ + 6O^{--} + N_2$

This suggests that these actions may take place as follows:

In (*e*) the hydrogen and the oxygen atoms separate in the form of ions (as H^+ and O^{--} respectively) and leave the nitrogen atom as an ion charged with as many charges as will make the sum of the negative charges equal to the sum of positive charges on all these products: since the three O^{--} together are charged with six negative charges, and the H^+ with one positive charge, the N must be charged with $6 - 1 = 5$ positive charges. Then the free electrons act upon the N^{5+} ion ($5\ominus$ upon 1 N^{5+}) to form the free element, N_2° while the H^+ and O^{--} ions remain temporarily or permanently as free ions.

In the other reactions above, *a*, *b*, *c*, and *d*—we find it convenient to assume that the reactions take place as in (*e*),—namely that HNO_3 is ionized into elemental ions—and to consider that the free electrons react only with the N^{5+} ion while the other ions are not affected by electrons. According to the number of electrons in the equations above, the N^{5+} ion will be changed to N^+, N^{++}, N^{+++}, or N^{++++} in equations (*a*) to (*d*) respectively. *Vice versa*, the number of electrons required in a change is equal to the algebraic difference between the valence of N in the original and in the resulting compound.

Finally, the ions temporarily formed will recombine as far as possible to form those combinations which have little or no tendency to dissociate. Thus, H^+ and O^{--} ions will combine to H_2O until one or the other of these kinds of ions is exhausted; N^{4+} will combine with $2O^{--}$ to form NO_2; N^{++} will combine with O^{--} to form NO; etc. Hence, the *complete* changes (*a*) to (*e*) above are presented by the following equations:

(*a*) $(H^+, N^{5+}, 3O^{--}) + 1\ominus + H^+ = NO_2 + H_2O$
(*b*) $(H^+, N^{5+}, 3O^{--}) + 2\ominus + 2H^+ = HNO_2 + H_2O$
(*c*) $(H^+, N^{5+}, 3O^{--}) + 3\ominus + 3H^+ = NO + 2H_2O$

(*d*) $2(H^+, N^{5+}, 3O^{--}) + 8\ominus + 8\,H^+ = N_2O + 5H_2O$

(*e*) $2(H^+, N^{5+}, 3O^{--}) + 10\ominus + 10H^+ = N_2 + 6H_2O$

We find in the same way, that every compound which is the essential "actor" in an oxidation or in a reduction action contains one particular element which—like N in HNO_3—changes its polar[1] valence, and which is the particular element oxidized or reduced. Hence, it is important to know how to "figure out" the *elemental ions* of such compounds, and for this purpose the following suggestions are given here.

1. In the ionization of compounds, hydrogen and the basic metals of salts always form ions with positive charges corresponding to their valences.

2. Oxygen generally forms the bivalent anion O^{--}, or together with hydrogen it forms the monovalent hydroxyl ion, OH^-. The chief exception to this rule is met with in peroxides—*e.g.*, H_2O_2 and Na_2O_2—in which oxygen is present as O^- because there can be no doubt that the hydrogen would form $2H^+$, or the sodium $2Na^+$.

If we know what ions the cations and the oxygen in a ternary electrolyte form, then we can calculate the polar valence of the third element by using only the simple rule that in ionization positive and negative charges are always formed in equal numbers. This has been shown with HNO_3 above, and may be shown again with the following substances:

(*a*) $KMnO_4$: the oxygen will form four bivalent anions, $4O^{--}$. Thus eight negative charges will have been formed with these $4O^{--}$ and eight positive charges formed simultaneously: the potassium atom takes one of these to form K^+, and seven positive charges must be taken by the only remaining atom, which is Mn. Hence the polar valence of the latter is Mn^{7+}, and the elemental ions of $KMnO_4$ are, K^+, Mn^{7+}, $4O^{--}$.

(*b*) $K_2Cr_2O_7$: $7O^{--}$ ions will evidently be formed, hence 14 positive charges must be accounted for. The $2K^+$ take two of them, and hence the 2Cr atoms take 12, or each Cr takes 6 positive charges. The elemental ions of $K_2Cr_2O_7$ are: $2K^+$, $2Cr^{6+}$, $7O^{--}$.

In ternary compounds containing a halogen or sulphur in place of oxygen, it is logical to assume that the halogen forms the well known anions—*e.g.* Cl^-, Br^-, I^-, and sulphur the ion S^{--}. The following examples illustrate this.

NH_4Cl: on complete ionization of this compound, four H^+ will be formed, and since Cl takes only one of the four negative charges formed simultaneously, the N must take the remaining three. Thus the elemental ions of NH_4Cl are: N^{3-}, $4H^+$, Cl^-.

Na_3AsS_4: the sodium atoms form $3Na^+$; the sulphur atoms form $4S^{--}$; hence the arsenic atom will be charged with $8 - 3 = 5$ positive charges.[2]

The Forming of Any Compound from Elemental Ions in a Mixture.—Just as any polyatomic compound may be resolved—or considered to be resolved—into its elemental ions, so any compound may be formed by the assembling of the necessary elemental ions. Thus when aluminum is formed in or introduced into a solution containing NaOH, the aluminum ion, Al^{+++}, will appear as $NaAlO_2$: this is evidently formed from $Na^+ + Al^{+++} + 2O^{--}$. Similarly, pentavalent arsenic will appear in a solution of NaOH in the form of Na_3AsO_4: this is formed by the union of $3Na^+ + As^{5+} + 4O^{--}$. Again, in the reduction of nitrate ion to ammonia in acid solutions (HCl), the nitrogen will finally be present as NH_4Cl: this is formed by the union of $N^{3-} + 4H^+ + Cl^-$.

[1] Since we must distinguish between positive and negative valences, these valences have been designated as *polar* valences.

[2] It is not intended to convey the idea that any large fraction of a ternary substance exists in the form of separate elemental ions: it is merely intended to show that it must ionize in a manner equivalent to what was shown above. The fraction of a substance present in the form of elemental ions is undoubtedly very small, but as this small amount is used up by reaction, other portions are ionized immediatedly, and thus progressively all of the material will be ionized.

It should be realized that all the necessary atoms for such compounds are *available in the form of elemental ions*, and need merely to be added together. They may not be present as *free* ions in any large amount, but they are obtainable by the ionization of their compounds which are present. Thus, the O^{--} needed for $NaAlO_2$ is not present as such, but is obtained from OH^- or from H_2O; when thus obtained, the whole complex (OH^- or H_2O) may be added to the left side of the equation, and the unused ions (H^+) left temporarily as *free* ions on the right side.

General directions for writing equations with polyatomic oxidizing or reducing agents are as follows: (1) Write—in the form of elemental ions—the formula for the compound of the element to be oxidized, putting it on the left-hand side of the equal sign, and put on the other side, the "elemental ion" formula of the resulting compound of the oxidized element. (2) Add to the right side, as many electrons as correspond to the valence-change of the oxidized element. For a "check" method of estimating the number of electrons, see the next paragraph. (3) Ascertain what other ions will be required to form final stable compounds of all the elemental ions in the original compound of the oxidized element, and add these ions—or the compounds from which they are obtainable by ionization—*to both sides* of the equation, placing together the ions of all compounds which naturally belong together

Thus, if the original compound of the oxidized element is $AsCl_3$, and the As is changed to H_3AsO_4, then we put (As^{3+}, $3Cl^-$) on the left side and ($3H^+$, As^{5+}, $4O^{--}$) on the right side, as per (1) above. Then we add $5 - 3 = 2$ electrons on the right side, as per (2) above, and finally we secure $3H^+$ for H_3AsO_4 and $3H^+$ more for the $3Cl^-$—total $6H^+$, and $4O^{--}$: or it might be better to secure $4H_2O$, and to leave $2H^+$ on hand. In the latter case, the equation obtained would be—

$$AsCl_3 + 4H_2O = H_3AsO_4 + 2H^+ + 2\ominus + 3HCl$$

For elements that are to be reduced, the corresponding equations are derived in the same manner except that the electrons are to be placed on the left side.

Thus for the reduction of $K_2Cr_2O_7$ to $Cr_2(SO_4)_3$, we obtain by this procedure:

$$(2K^+,\ 2Cr^{6+},\ 7O^{--}) + (14H^+,\ 7SO_4^{--}) + 6\ominus = (2Cr^{3+},\ 3SO_4^{--}) + 7H_2O + K_2SO_4 + 3SO_4^{--}$$

The equation for the reaction between any such polyatomic oxidizing (or reducing) agent with any particular reducing (or oxidizing) agent is obtained by the general procedure illustrated in the last example on p. 692, and it consists of the following: multiply either one or both of the equations for the single actions of the oxidizer and reducer *by factors* which will make the number of electrons in one equal to those in the other; add the resulting equations, and insert such other ions to both sides as may be present and necessary to "couple up" all ions. For illustrations of this procedure, see particularly the paragraphs below headed "Nitrogen."

Simplified Method for Writing Equations for a Single Oxidizer or Reducer. (Second Method for Estimating Free Electrons Involved).—(1) Express by their common formulas the compounds, free elements, and ordinary ions used or produced in a reaction, writing ions with their proper electric charges, but whole compounds and free elements without any charges. (2) See that every atom which is introduced on one side appears also on the other. (3) Take the algebraic sum of the ionic charges *shown on all the ions* on each side of the equation and add on the proper side as many electrons as are necessary to balance the two sums.

Condition (3) above presents a second method for estimating the number of electrons in the action of an oxidizer (or reducer) and this method enables us to do

without the elemental ionizing of compounds. We consider the compounds or ion radicals simply with regard to their *electrical condition as a whole* which is *zero* for distinct compounds, such as H_2O, HNO_3, etc., or the usual ionic charges for the ordinary ions such as NO_3^-, MnO_4^-, etc.—and we make the difference between the algebraic sum of all *apparent* electric charges on the left of the equation *equal* to that on the right by inserting the necessary free electrons. If these are to be added to the right, the change consists of oxidation; if on the left, the change is reduction. For an illustration, see the equations below on this page.

This method is to be used particularly when the elemental ionizing of compounds is bothersome *e.g.*, with carbon compounds. For illustration see below, under "Carbon" (p. 705 *et seq.*).

Writing of Separate Equations for Oxidizer and Reducer is both Important and Simple.—The proof that the substance oxidized and the substance reduced react independently of each other except with respect to the free electrons passed from the former to the latter has made it possible to study and describe their properties and relations much more definitely than was possible otherwise: this separation of the two actions is the key to the whole modern study and treatment of this subject of oxidation and reduction. Hence, throughout this chapter, the reactions of the substances oxidized and of those reduced are presented separately, and it is shown that reactions between any particular individuals are merely the algebraic sums of their separate reactions. The reader should realize the importance of studying the individual reactions of oxidizers or reducers, and to practice obtaining their combined reactions by adding, algebraically, the individual reactions previously obtained.

The writing of the individual reaction is after all a very simple matter because it is almost immaterial in what form the symbols of the substances are written. For illustration let us try to write the equation for the oxidation of $SnCl_2$ to $SnCl_4$. We may consider that this is simply a change of Sn^{++} to Sn^{4+}, and hence write the equation thus

$$Sn^{++} = Sn^{4+} + 2\ominus$$

Or we may write the equation with both chlorides, adding the 2 Cl^- required in the form of free ions, thus

$$SnCl_2 + 2Cl^- = SnCl_4 + 2\ominus$$

Or we may add the $2Cl^-$ in the form of 2HCl, thus

$$SnCl_2 + 2HCl = SnCl_4 + 2H^+ + 2\ominus$$

All three equations are equally correct and useful.

An application of the "Simplified Method" above may be made here: note that all substances are written so as to express electric conditions correctly. Note also that the number of free electrons necessary to balance the sum of the electric charges shown on the free ions on the two sides of each equation is $2\ominus$ in all three equations. To learn how the latter is obtained, see the last equation above: here the algebraic sum of the charges on the substances on the left is *zero plus zero* (= 0); that for the substances on the right is zero plus two positive (= 2^+). Hence, we must add $2\ominus$ to the right side.

Oxidizing Powers of Different Oxidation Stages of an Element.—At first sight it might appear to us that the different oxidation stages of an element with three or more oxidation stages *e.g.*, nitrogen—should have oxidizing powers in the

order of their oxidation stages, that is, NO should be a stronger oxidizing agent that N_2O, HNO_2 stronger than NO, etc. In some cases this is true, but it is not true in general although the formation of the higher oxidation stages usually takes place by oxidation of lower stages. The above erroneous notion is probably due to the analogy which most of us draw between the "raising" of an element to different oxidation stages and the lifting of an object to higher levels: this analogy may be followed out so as to correspond to the facts observed.

For this purpose, we need merely consider that the object instead of remaining at the highest point to which it is raised (and at which it would have the correspondingly higher potential energy than at the lower oxidation stage), may have dropped to a lower level on the other side of an obstacle over which it had to be raised: in its final position it may then have a potential of position even lower than that from which it was last raised. Thus completed, this analogy may serve to explain why higher oxidation stages are not necessarily possessed of a greater potential to return to lower stages—or in other words, are not necessarily stronger oxidizing agents than lower oxidation stages; and correspondingly, lower oxidation stages are not necessarily stronger reducing agents than higher oxidation stages. Thus we find that ammonia (in which the nitrogen is reduced to the N^{3-} stage) is not as strong a reducing agent as hydroxylamine (in which nitrogen is reduced only to the N^{-} stage), and that perchloric acid (in which chlorine is in the Cl^{7+} stage) is not as strong an oxidizing agent as chloric acid (in which chlorine is in the Cl^{5+} stage).

The chemical fact which in these examples corresponds to the dropping of the raised object to a lower level on the other side of an obstacle over which it had to be raised is the formation of a relatively stable combination of atoms after the electronic oxidation—*i.e.*, the valence change in the N or in the Cl respectively in the examples quoted above—has taken place. In these examples, the stable combinations of atoms are NH_3 and $HClO_4$ respectively. The word stable designates compounds which have a less tendency to dissociate into the substances from which they have been formed than corresponds to the energy expended in forming them, and the formations of such compounds always involves a loss of free energy in the reacting mixture. The latter corresponds to the "dropping of the object to a lower level" in the above analogy.

Potentials of Changes Involving Hydrogen and Oxygen Ions Vary with Acidity of Solutions.—The potentials of polyatomic oxidizing or reducing agents which in ionizing form O^{--} or H^{+}, or combine with them to form their final stable compounds, are affected by the concentration of H^{+} (or OH^{-}) in the solution because either O^{--} or H^{+} is formed or used up in excess of the other, and this "excess" of one or the other must be given to, or obtained from, the rest of the solution. The ease or difficulty of obtaining O^{--} or H^{+} from the rest of the solution (or giving them to the rest of the solution) naturally depends directly upon the concentrations of the free O^{--} or H^{+} in the solution, and the relation is the following: the potential with which such a substance tends to be oxidized (a reducing agent!) is greater in *alkaline* solutions than in *neutral*, and is *least* in *acid* solutions. This is due to the fact that all such reducing agents use up an excess of O^{--} over H^{+}, or produce in the change, an excess of H^{+} over O^{--}.

For example, the tendency of arsenic trichloride to be oxidized to the next higher oxidation stage of arsenic is least in acid solutions, greater in neutral solutions, and greatest in alkaline solutions. The equation for the change is

$$(As^{+++}, 3Cl^{-}) + 4H_2O = (3H^{+}, As^{5+}, 4O^{--}) + 2\ominus + 5H^{+} + 3Cl^{-}$$

This equation shows that the action produces free H_2^+, and these must be added to the rest of the solution: the disposition of these H^+ will naturally be easier in an alkaline solution in which they combine with OH—or in other words, in which the H^+ concentration is low—than in an acid solution in which the H^+ concentration is high. This effect of the H^- concentration is expressed more definitely by the following mass law relation between the concentrations of all substances present when these materials are in a solution by themselves and the above reaction has attained equilibrium: the concentration of the electrons then is proportional to the potential. To get this mass-law relation at equilibrium, we must take the product of the concentrations of the substances on the left of the equation above—raising each factor to the power equal to the coefficient of its substance in the equation above; then we secure in the same manner the corresponding product of the concentrations of the substances on the right, and we multiply the latter by a *constant*, and put the two products equal to each other. Thus we obtain:

$$[As^{+++}] \times [Cl]^3 \times [H_2O]^4 = [H_3AsO_4] \times [H^+]^5 \times [Cl^-]^3 \times [\ominus]^2 \times (\text{Const.})!$$

Here the square braces around the substances designate their concentrations.

Since the electron concentration is proportional to the "potential" or "voltage" with which this reaction tends to take place, and which this mixture would produce if used with a platinum pole as one pole of a battery cell, we will divide the whole expression by all factors on the right except the electron concentration, and thus obtain:

$$\frac{[As^{+++}] \times [Cl]^3 \times [H_2O]^4}{[H_3AsO_4] \times [H^{++}]^5 \times [Cl^-]^3 \times (\text{const.})} = [\ominus]^2$$

It is evident from this expression that any decrease in the value of H^+ increases the value of the electron concentration, and thus raises the voltage (or position) which this "pole" would have in our table: in other words, it would increase its tendency to change to the oxidized state.

A familiar illustration of the corresponding effect upon the potential with which a substance tends to be reduced (an oxidizing agent) is found in the action of the nitrate ion in acid and alkaline solution respectively: in both, the nitrate ion may be reduced to the nitrite ion, according to the equation

$$(N^{5+},\ 3O^{--}) + 2\ominus = (N^{3+},\ 2O^{--}) + O^{--}$$

or

$$(NO_3)^- + 2\ominus = (NO_2)^- + O^{--}$$

In acid solutions, the concentration of free O^{--} is extremely small, but in alkaline solutions, the O^{--} concentration is relatively large. This greater concentration of O^{--} ions in the alkaline solution produces a greater *opposing* effect than its lesser concentration in the acid solution, and hence a solution of HNO_3 (*i.e.*, NO_3^- in acid solutions) is a much stronger oxidizing agent than a solution of $NaNO_3$ (*i.e.*, NO_3^- in neutral or alkaline solution).

Hence, the general rule that *oxidizing agents are strongest in acid solutions, and reducing agents strongest in alkaline solutions.* However, this applies only to reactions of oxidizing or reducing agents in which H^+ or OH^- ions are involved; while reactions such as the following do not change their "potentials" when the H^+ or OH^- concentrations of their solutions are changed:

$$Cl_2^\circ + 2\ominus = 2Cl^-$$
$$MnO_4^- + 1\ominus = MnO_4^{--}$$

For a more extensive consideration of these effects, see the section on "Halogens" below.

Substances which Act Simultaneously as Oxidizers and as Reducers in the Same Mixtures.—A very striking example of oxidation-reduction reactions is found in the case of a number of substances such as NO_2 in cold water, free elements (halogens, sulphur, phosphorus) in alkaline solutions, hypochlorites in either acid or alkaline solutions, etc., in which some molecules of a substance change to a more oxidized state while other molecules of the same substance change to a more reduced state. Thus NO_2 dissolves in cold water and changes according to the equation

$$2N^{4+}O_2 + H_2O = HN^{3+}O_2 + HN^{5+}O_3$$

The valences of the nitrogen in the different compounds are marked in this equation, and these marks show that one NO_2 is reduced to HNO_2 while the other is oxidized to HNO_3, the amount of reduction (addition of $1\ominus$ to NO_2) being equal to the amount of oxidation (liberation of $1\ominus$ from $1NO_2$).

Again, chlorine dissolves in NaOH solution and reacts according to the equation

$$Cl_2^\circ + 2NaOH = NaCl^- + NaOCl^+ + H_2O.$$

The "marked" valence on the chlorine atoms shows that $1Cl^\circ$ is reduced to Cl^- (with addition of $1\ominus$) while $1Cl^\circ$ is oxidized to Cl^+ (with liberation of $1\ominus$).

In order to understand how these reactions are related to the ordinary oxidation-reduction reaction, we must realize, first of all, that the force, potential, or voltage with which a substance tends to change its valence depends upon the *change* undergone, *i.e.*, the whole transformation expressed by the equation—and not merely upon the original substance. Thus the change from Cl° to Cl^- has a potential of 0.65 volt, while that from Cl° to Cl^+ (or HOCl) in acid solution is only 0.37 volt, or in other words, as an oxidizing agent the potential of chlorine is 0.65 volts, but as a reducing agent in acid solution, its potential is only 0.37 volts. Similarly, any element in an intermediate stage of oxidation will exert one potential to pass to a higher stage and another potential to pass to a lower stage.

Furthermore, we must recall the fact that, in order that a reducer may actually react with a particular oxidizer, the potential of the reducer must be greater than that of the oxidizer (according to the method of reckoning potentials employed in this chapter). In this connection, see the diagram given in the "Note on Table of Oxidation Changes."

It may now be seen why the same substance may act simultaneously as oxidizer and as reducer: to do this, it need only have the potential of its change to a higher oxidation stage greater than the potential of its change to a lower oxidation stage. Thus, in alkaline solutions, chlorine changes from Cl° to Cl^+ (*i.e.*, ClO^- ion) according to the following equation

$$Cl_2^\circ + 4(OH)^- = 2(Cl^+O^{--}) + 2\ominus + 2H_2O \quad \text{(potential 1.57 V.)}$$

while its change from Cl° to Cl^-, which takes place according to the equation

$$Cl_2^\circ + 2\ominus = 2Cl^-$$

has the potential of 0.65 volts. Hence these two reactions have their potentials *properly related to act together* (see diagram—"Notes on Table") and their combined reaction, as always, is the sum of the separate changes of the oxidizer and reducer (with the inactive $2Na^+$ added to both sides).

$$Cl_2^\circ + 2NaOH = NaOCl + NaCl + H_2O.$$

General considerations of this kind of reactions show that the general relations between the potentials of the oxidizing and of the reducing changes should be as shown: for this particular example, the potentials obtained or calculated from measurements confirmed our general conclusions. Corresponding measurements have not been made, so far, on all other examples, but it is quite certain that the same general relations must exist in all cases. Thus for the reaction between NO_2 and cold water, the oxidation change

$$NO_2 + OH^- = HNO_3 + 1\ominus$$

must have a greater potential than the reduction change

$$NO_2 + H^+ + 1\ominus = HNO_2$$

Since it was shown in the preceding paragraph that reactions which involve the ions of water (H^+ or OH^-) change their potentials when the solutions are changed from acid (great H^+ and small OH^- concentrations) to alkaline reaction (small H^+ and great OH^- concentration), it follows that the above relation between the potentials of the oxidizer and the reducer may be reversed if solutions with a different H^+ concentration are used. Such is actually the case with Cl_2°: in acid solutions, the oxidation product of chlorine is un-ionized HClO, and the formation of this substance from Cl_2° in acid solution (few OH^-) takes place according to the equation—

$$Cl_2^\circ + 2OH^- = 2HOCl + 2\ominus$$

The potential of this change is 0.37 volts, while the potential of the corresponding change in alkaline solution (see above) is 1.57 volts. But the potential of the reduction of chlorine to chloride—

$$Cl_2^\circ + 2\ominus = 2Cl^-$$

is evidently not dependent on the H^+ or OH^- concentration, and is still 0.65 volts. The former equation here would have a place in our Table below that of the latter, and hence these two reactions could not take together (See diagram-note on Table, p. 691, and correspondingly, in acid solutions, free chlorine remains practically unchanged. For further consideration of these particular relations, see section headed below "Halogens."

Definition of Normal Solution of an Oxidizer.—A normal solution of an oxidizer (or reducer) contains in one liter volume as much of this substance as amounts to its formula-weight, in grams, divided by the number of free electrons which appear in the equation for its separate action. Thus, a normal solution of $KMnO_4$ contains one-fifth of 158.04 g. per liter, because it reacts according to the equation

$$(K^+, Mn^{7+}, 4O^{--}) + 8H^+ + 5\ominus = K^+ + Mn^{++} + 4H_2O$$

A normal solution of oxalic acid contains one-half of 126.06 g. per liter, because it reacts according to the equation

$$(COOH)_2 + O^{--} = 2CO_2 + H_2O + 2\ominus$$

Differential Oxidation.—Since no reaction will take place unless the potential of the change of the reducer is greater than the potential of the change of the oxidizer, it follows that we may so choose the latter as to affect only one of several reducers in a mixture. Thus, if it is desired to oxidize iodides only when bromides also are present, we can accomplish this by using HNO_2 because the potential of HNO_2, changing to lower oxidation stages is about 1.2 volts while that of the

$$2Br^- = Br_2^\circ + 2\ominus$$

change is 0.92 volt, and with this relation between the potentials there can be no reaction. However, the potential of the change:

$$2I^- = I_2^\circ + 2\ominus$$

which is 1.46 volts, is so related to the potential of the above action of HNO_2 as to bring about a reaction. Hence, HNO_2 will change the iodide to free iodine, but will not affect the bromide.

Another way to accomplish the same result is to use $KMnO_4$ with differently acidified solutions, because the potential of the change

$$(K^+,\ Mn^{7+},\ 4O^{--}) + 8H^+ + 5\ominus = K^+ + Mn^{++} + 4H_2O$$

decreases with increase of H^+ ion concentration: with such an H^+ ion concentration as is obtained in acetic acid plus sodium acetate, the potential of the permanganate is great enough to react with iodides only, *i.e.*, its potential is less than the potential of the iodide-iodine change, 1.46 volts, but greater than the potential of the bromide-bromine change, 0.92 volts; if the solution is moderately acidified with H_2SO_4 or HNO_3 bromides are oxidized, but chlorides only to a negligible extent (potential between 0.92 volts for bromides and 0.65 volts for chlorides) But with large additions of H_2SO_4 or HNO_3, the oxidation of chlorides also is appreciable.

PART II

Details of Oxidation-Reduction Behavior of the Common Elements.—The remainder of this section will present under each element the special facts shown by them in oxidation-reduction reactions. The elements will be considered in the order of their positions in the periodic system.

Sodium, Potassium, Magnesium, Calcium, Strontium, Barium, and Aluminum.—These metals exhibit a great tendency to pass to the oxidized state: they are strong reducing agents, usable at ordinary or room temperatures (see Table, Nos. 1 to 5). They undergo only the one valence change illustrated by the following equations:

$$Na^\circ = Na^+ + 1\ominus$$
$$Mg^\circ = Mg^{++} + 2\ominus$$
$$Al^\circ = Al^{+++} + 3\ominus$$

Since the alkali metals—sodium and potassium—react violently with water, they can be employed for the reduction of substances in aqueous solutions only in the form of amalgams. Calcium, strontium, and barium also are best employed in the form of amalgams, but magnesium and aluminum are employed direct—usually in a finely divided form such as filings, etc. For the reduction of substances in non-aqueous mixtures—such as solutions in alcohol, ether, benzene, etc., the alkali metals also are employed directly, *i.e.*, as such.

Aluminum is frequently used as a reducing agent in sodium hydroxide solutions because aluminum ion (Al^{+++}) in sodium hydroxide solutions unites with Na^+ and $2O^{--}$ to form the compound $NaAlO_2$ which is soluble. For an illustration of the use of this reducing agent, see "Nitrogen" below.

Copper, Silver and Gold.—These metals have a low tendency to change to their simple ions, *i.e.*, the ions formed from solutions of their simple salts such as chlorides, nitrates, etc. (see Table, Nos. 21 and 24: the corresponding place for gold would be between Nos. 28 and 29). Hence they are very feeble reducing agents, and are practically never used as such.

In solutions in which the ions of these metals form complex ions, *i.e.*, in ammonia, or potassium cyanide solutions, most of the simple ions of these metals are combined with other ions and hence the reverse tendency of these metals to change to the metallic form is lessened so much as to give these metals a much greater reducing power (or a higher position in the table). However, no special use is made of this fact.

In practice, a few examples of monovalent copper ion, Cu^+, are met with. Thus cuprous chloride is used in gas analysis as an absorbent for CO. It is produced by boiling cupric chloride with metallic copper, and in this reaction $1Cu^{++}$ is reduced to Cu^+ while 1 atom of copper metal is oxidized to Cu^+, according to the equations:

$$Cu^{++} + 1\ominus = Cu^+$$
$$Cu^\circ = Cu^+ + 1\ominus$$

On adding these equations and inserting the inactive Cl^-, we obtain:

$$CuCl_2 + Cu^\circ = 2CuCl$$

Since cuprous chloride is but slightly soluble in water, it is made and employed in a solution containing much hydrochloric acid. It is also soluble in ammonia. In both cases, the increased solubility is due to the extensive union of Cu^+ with other ions to form complex ions (*e.g.*, NH_3Cu^+ and $CuCl_2^-$ respectively).

In cyanide solutions, copper is also present in the cuprous form. Its reduction from cupric to cuprous ion takes place by the oxidation of the cyanide ion, and since the whole action is met in the treatment of a cupric salt with KCN, the equations for the whole change are here given:

$$(1)\ CuSO_4 + 2KCN = Cu(CN)_2 + K_2SO_4$$
$$(2)\ 2\ Cu(CN)_2 = 2CuCN + (CN)_2$$
$$(3)\ KCN + CuCN = KCu(CN)_2$$

Only (2) is an oxidation-reduction action. To understand it we need to consider that, on ionizing, $Cu(CN)_2$ gives $Cu^{++} + 2(CN)^-$ and that $1(CN)^-$ gives up its negative charge to Cu^{++} reducing the latter to Cu^+.

Zinc, Cadmium, Mercury.—This group includes the most commonly used reducing agent—zinc. It is used with either dilute sulphuric acid or sodium-hydroxide solution, but the latter are not for the purpose of reacting with it to evolve hydrogen: they serve to prevent the formation of a layer of $Zn(OH)_2$ upon the surface of the metal if the action of the reduced substance uses up hydrogen ion. For illustration, see under "Nitrogen," "the reduction of *nitrates* to ammonia." When hydrogen is not used up by the reduced substance, then an acid or sodium hydroxide is not needed—as shown in the following equations for the reduction of ferric compounds to ferrous. In this action we have the zinc changing as follows:

$$Zn^\circ = Zn^{++} + 2\ominus$$

while the ferric ion changes thus:

$$Fe^{+++} + 1\ominus = Fe^{++}$$

Evidently, one Zn produces enough electrons for two ferric ions, hence they change in the ratio Zn:2 Fe^{+++}. Then the sum of the two simultaneous changes is expressed by:

$$Zn^\circ + 2Fe^{+++} = ZN^{++} + 2Fe^{++}$$

Adding the inactive anions (*e.g.*, SO_4^{--}) we obtain

$$Zn^\circ + Fe_2(SO_4)_3 = ZnSO_4 + 2\ FeSO_4$$

Cadmium is employed in place of zinc if a less energetic reducing agent is desired. Its action is just like that of zinc, except that it cannot be used in alkaline solutions because $Cd(OH)_2$ does not react to form a soluble compound with NaOH as $Zn(OH)_2$ does.

Mercury exerts a very small tendency to be oxidized (see Table, No. 23) hence it is never used as a reducing agent. Since it is easily reduced from its ion form (Hg^+ or Hg^{++}) its compounds are used occasionally as oxidizing agents. Thus in purifying mercury, metals such as zinc, iron, etc., are removed by treating the impure mercury with a solution of mercurous nitrate, which converts the zinc or iron to ions while an equivalent amount of Hg^+ is reduced from the solution, as shown by the following equations:

$$Zn^\circ = Zn^{++} + 2\ominus$$
$$2Hg^+ + 2\ominus = 2Hg$$

Adding these equations, and inserting the inactive NO_3^- ions, we obtain

$$Zn^\circ + 2HgNO_3 = Zn(NO_3)_2 + 2Hg$$

Tin and Lead.—These metals have practically the same electromotive tendency for the change from the metal form to the bivalent ion (see Table, Nos. 15 and 16). They are milder reducing agents than cadmium. On account of the proximity of the potentials of lead and tin, lead is used when antimony is to be reduced to the metal form out of solutions containing both tin and antimony: the potential of antimony is much less than that of lead (see Table, No. 18), while that of tin is practically equal to that of lead hence antimony is entirely reduced by the action of lead while practically no tin is reduced. The equations for the action are:

$$3Pb^\circ = 3Pb^{++} + 6\ominus$$
$$2Sb^{+++} + 6\ominus = 2Sb^\circ$$

adding these equations, and inserting the inactive anions (Cl^-), we obtain:

$$3Pb^\circ + 2SbCl_3 = 3PbCl_2 + 2Sb^\circ$$

Both tin and lead exist also in the tetravalent form, and the potentials of the changes from bivalent to tetravalent ions are much less than those of the changes from metals to bivalent ions (see Table, Nos. 19 and 35). Hence the action of even mild reducing agents such as metallic lead or tin serves to reduce tetravalent tin to the bivalent form, as shown by the equation

$$Sn^{++++} + Sn^\circ = 2\ Sn^{++}$$

Here tin furnishes both the oxidizing and the reducing agent.

Stannous chloride solution acidified with hydrochloric acid is frequently employed as a reducing agent. It changes in accordance with the equation

$$Sn^{++} = Sn^{4+} + 2\ominus$$

or

$$SnCl_2 + 2\ Cl^- = SnCl_4 + 2\ominus$$

and the potential of this change is given in the Table, line 19: from the latter it is evident that any of the substances in the right hand column and below line 19 will react with it. Thus it is seen that it will reduce mercurous compounds to mercury and hence it will reduce mercuric compounds all the more readily—either to the mercurous stage or to free mercury. The corresponding equations follow:

$$SnCl_2 + 2Cl^- = SnCl_4 + 2\ominus$$
$$2HgCl_2 + 2\ominus = 2\ HgCl + 2\ Cl^-$$

Adding, we obtain

$$SnCl_2 + 2HgCl_2 = SnCl_4 + 2HgCl$$

If the Hg^{++} is changed to Hg°, the equation for the change is evidently

$$HgCl_2 + 2\ominus = Hg^\circ + 2Cl^-$$

and this combined with the above equation for the change of Sn^{++} gives

$$SnCl_2 + HgCl_2 = SnCl_4 + Hg^\circ$$

The reduction of ferric salts to ferrous salts is frequently accomplished by means of stannous chloride. Since the mixture will contain a large amount of Cl^- we may consider the iron salts to be chlorides, and hence the reaction for the change from ferrous to ferric is

$$(Fe^{+++}, 3Cl^-) + 1\ominus = (Fe^{+++}, 2Cl^-) + Cl^-$$

To combine this with the equation for the change of stannous chloride above, we must multiply the last equation by *two;* then on adding the resulting equation to the one for the stannous chloride, we obtain

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$

Stannous oxide is soluble in caustic soda with the formation of the compound Na_2SnO_2, sodium stannite. The corresponding stannic compound, Na_2SnO_3, also exists, and is a fairly stable compound. The change from stannite to stannate naturally takes place according to the equation

$$Na_2SnO_2 + 2\ OH^- = Na_2SnO_3 + H_2O + 2\ominus$$

This solution of sodium stannite is a fairly strong reducing agent, as shown by the fact that it reduces copper hydroxide, bismuth hydroxide, etc., to the free metals. On boiling the solution reacts to form tin and Na_2SnO_3.

In other words, one molecule out of two of the stannite acts as the reducing agent while the other acts as the oxidizing agent. The general relation of the potentials which makes this possible was given in Part I, last article. The equations for the reduction of the tin are:

$$Na_2SnO_2 + 2H_2O + 2\ominus = 2Na^+ + (2H_2O + 2O^{--}) + Sn^\circ$$
$$= 2NaOH + 2OH^- + Sn^\circ$$

The equation for the reduction of $Bi(OH)_3$ is

$$Bi(OH)_3 + 3\ominus = Bi^\circ + 3OH^-$$

The combining of either one of the two last equations with the preceding equation for the oxidation of Na_2SnO_2 to Na_2SnO_3 is a simple matter and hence need not be given here.

The most important oxidation stages of lead and their behavior may be observed in the storage battery.

The lead storage battery has for its chemically active substance spongy lead at the negative pole and a brownish-black powder, PbO_2, at the other pole. These

materials are held by a "skeleton" of lead which remains unchanged except on the surface. The liquid in which the poles are immersed is dilute sulphuric acid. The change at the negative pole, when the cell is furnishing current is

$$Pb^{\circ} = Pb^{++} + 2\ominus$$

The Pb^{++} immediately combines with SO_4^{--} because $PbSO_4$ is practically insoluble; hence the whole change is

$$Pb^{\circ} + SO_4^{--} = PbSO_4 + 2\ominus$$

The change at the positive pole is

$$(Pb^{4+}, 2O^{--}) + 2\ominus = Pb^{++} + 2O^{--}$$

The free oxygen ions, as soon as formed, will combine with H^+ present in the electrolyte; and the Pb^{++} will unite with SO_4^{--}; hence the whole change at the positive pole is

$$(Pb^{4+}, 2O^{--}) + 4H^+ + SO_4^{--} + 2\ominus = PbSO_4 + 2H_2O$$

The change for the cell as a whole is obtained by adding these equations for the two pole changes:

$$Pb^{\circ} + PbO_2 + 4H^+ + 2SO_4^{--} = 2PbSO_4 + 2H_2O$$

It is evident that when the cell is furnishing current, lead at the negative pole is oxidized, and lead peroxide at the positive pole is reduced.

When the cell is recharged, the above changes take place in the reverse sense.

Lead peroxide in dilute sulphuric acid is a strong oxidizing agent (see its position in the Table, No. 35, and note that the substances in the lower part of the right hand column are all strong oxidizing agents). The oxidizing tendency of PbO_2 is shown in the fact that it gives up oxygen gas on heating and changes to PbO.

Carbon.—It is not intended to discuss here any representative set of the many compounds of carbon which take part in oxidation-reduction reactions, nor even a partial list of those which are reducing agents—although the latter are very important, particularly in photography, but to consider merely the equations of the oxidation of a few compounds in order to show how such equations are to be arrived at.

In order to estimate the number of free electrons liberated when a carbon compound changes from one to another state of oxidation, we use the *second method*, in Part I, for the estimation of the number of electrons required for polyatomic substances, that is, we note

(*a*) That the original and the final compounds are usually not ionized—that is, they are electrically neutral.

(*b*) That *ionic* hydrogen (H^+) and *ionic* oxygen (O^{--} or OH^-) are used in the reaction—*i.e.*, when oxidizing agents other than free oxygen gas are used—and that the algebraic sums of their ionic charges are obtained as free electrons because all other substances are electrically neutral.

Hence, to figure out the equation for the oxidation of a carbon compound by an oxidizing agent other than free oxygen, add as many O^{--} and H^+ as may be necessary to form the final products, and add to the right side as many free $\ominus$ as is necessary to balance the algebraic sums of the ionic charges on the two sides of the equations.

Thus, when ethyl alcohol is oxidized to acetaldehyde, the equation for the change is

$$CH_3CH_2OH + O^{--} = CH_3CHO + H_2O + 2\ominus$$

or

$$CH_3CH_2OH = CH_3CHO + 2H^+ + 2\ominus$$

For the oxidation of aldehyde to acetic acid, the equation thus obtained is

$$CH_3CHO + O^{--} = CH_3COOH + 2\ominus$$

or

$$CH_3CHO + (2H^+, O^{--}) = CH_3COOH + 2H^+ + 2\ominus$$

For the oxidation of oxalic acid, the equation is

$$(COOH)_2 + O^{--} = 2CO_2 + H_2O + 2\ominus$$

or

$$(COOH)_2 = 2\,CO_2 + 2H^+ + 2\ominus$$

For the oxidation of formic acid, the equation is

$$HCOOH + O^{--} = CO_2 + H_2O + 2\ominus$$

or

$$HCOOH = CO_2 + 2H^+ + 2\ominus$$

For the oxidation of formalin to CO_2 and H_2O, which occurs in the disinfection of rooms in which some formalin is vaporized by the heat of reaction between another portion of formalin and permanganate, the equation is

$$H_2CO + 2O^{--} = CO_2 + H_2O + 2\ominus$$

The permanganate used for this purpose is reduced to MnO_2, hence, the equation for its reduction is

$$(K^+, Mn^{7+}, 4O^{--}) + 3\ominus = K^+ + (Mn^{4+}, 2O^{--}) + 2O^{--}$$

To combine the last two equations, we must multiply the last by 2 and preceding by 3: adding these equations, and noting that $KHCO_3$ will be the most stable combination in which K^+ will remain in this mixture, and that this is formed by the simple union of $K^+ + H^+ + O^{--} + CO_2$, we obtain

$$KMnO_4 + H_2CO = KHCO_3 + MnO_2$$

Since the oxidation of ethyl alcohol to aldehyde is usually accomplished by means of acidified bichromate, we will derive the complete equation for this change. The equation for the change of the bichromate is derived under chromium, and is here merely stated

$$(2Na^+, 2Cr^{6+}, 7O^{--}) + 6\ominus + 14H^+ = 2Cr^{+++} + 2Na^+ + 7H_2O$$

or

$$(2Na^+, 2Cr^{6+}, 7O^{--}) + 6\ominus + 7\,H_2SO_4 = Cr_2(SO_4)_3 + Na_2SO_4 + 7H_2O + 3SO_4^{--}$$

To combine the last with the equation for the change of ethyl alcohol to aldehyde given above, we multiply the latter by three in order to make the number of electrons formed equal to the number used up by one molecule of bichromate. Then adding the resulting equation to that for the bichromate, and eliminating $3H_2SO_4$ from both sides, we obtain

$$3CH_3CH_2OH + Na_2Cr_2O_7 + 4H_2SO_4 = 3CH_3CHO + Na_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$$

These examples may suffice to show how such equations are derived. It might be added that, if the oxidizing is done by gaseous oxygen—as in the burning of methane—no special device is needed to derive the equation, and the amount of oxidizing done is expressed directly by the number of oxygen atoms used up.

Another type of reaction which may be of special interest is the formation of chloroform from ethyl alcohol and hypochlorite of lime. Concerning the action of the latter, see below under "Halogens." The change of the ethyl alcohol results in the formation of the formic acid ion and of chloroform, which takes place according to the following equation:

$$CH_3CH_2OH + 3Cl^- + 3O^{--} = CHCl_3 + HCOO^- + 2H_2O + 8\ominus$$

The change in the hypochlorite is

$$(Ca^{++},\ 2O^{--},\ 2Cl^+) + 4\ominus = Ca^{++}\ Cl_2^- + 2O^{--}$$

Multiplying the latter by 4, the former by 2, adding, eliminating $6O^{--}$ and $6Cl^-$ from both sides, we obtain

$$2CH_3CH_2OH + 4Ca(OCl)_2 = 2CHCl_3 + Ca(COOH)_2 + 4H_2O + 2CaO + CaCl_2.$$

The 2CaO will naturally combine with $2H_2O$ to form $2Ca(OH)_2$

Nitrogen.—This element furnishes at once the two most important and generally used oxidizing agents, HNO_3 and HNO_2, and also two of the strongest reducing agents—hydroxylamine and hydrazine. We shall consider the action of nitric acid first.

The nitrogen in nitric acid and in nitrates is in the highest state of oxidation in which it occurs; and the nitrogen in ammonia or ammonium compounds is in the lowest state of oxidation, it cannot be reduced further. Between these two limits there are a number of oxidation stages, the order and relation of which is shown in the following table. Note that the free element occupies an intermediate position.

TABLE OF NITROGEN COMPOUNDS IN THE ORDER OF THEIR EXTENT OF REDUCTION FROM NITRIC ACID

Compounds	Elemental ions from theoretical ionization	Amount of reduction from HNO_3; electrons per 1 N
1. HNO_3, nitric acid (and nitrates)	H^+, N^{5+}, $3O^{--}$	0
2. NO_2, nitric peroxide	N^{4+}, $2O^{--}$	1
3. HNO_2, nitrous acid (and nitrites)	H^+, N^{3+}, $2O^{--}$	2
4. NO, nitric oxide	N^{++}, O^{--}	3
5. N_2O, nitrous oxide.	$2N^+$, O^{--}	4
6. N, nitrogen	N°	5
7. NH_2OH, hydroxylamine (or its salts)	N^-	6
8. NH_3(or NH_4OH), ammonia (or its salts)..	N^{---}, $3H^+$	8

From the position of nitric acid in the Table of Oxidation Changes, it is seen that nitric acid reacts with all substances in the left column above line 29. Technically, we say: all these substances in the left column from 29 up are *oxidized* by nitric acid. This includes all metals except gold, platinum, rhodium, and iridium.

The potential of the change of nitric acid to lower oxidation stages varies with the free H^+ concentration—from 1.0 volt for normal H^+ concentration to a value near 0.72 volt for large H^+ concentrations. The lowest potential obtained by measurement with concentrated HNO_3 is 0.72 volt.

Nitric acid is a slowly acting substance—it acts as though it had to overcome a reaction-hindrance. This coupled with the fact that its potential changes almost

directly with its H^+ concentration, irrespective of the reduction product formed, accounts for the fact that very dilute nitric acid frequently does not produce any oxidizing effects whatever.

When acting as an oxidizing agent, nitric acid is reduced to its various products named in the table above. It is seldom that, in any case, only one particular reduction product is formed; however, under particular conditions some particular product is mainly formed. The following general rule connects these conditions with the chief product formed in each case: The extent to which the nitrogen alone is reduced increases with the degree of dilution of the nitric acid and with the force of the reducing agent. For example:

conc. HNO_3 + copper gives NO_2
dil. HNO_3 + copper gives NO
dil. HNO_3 + zinc gives N
very dil. HNO_3 + zinc gives NH_3

The above rule and these examples serve as a means of predicting the extent of reduction of nitric acid in other mixtures.

The reactions for the formation of seven different reduction products of nitric acid are expressed by the following equations:

(*a*) $(H^+, N^{5+}, 3O^{--}) + 1\ominus + 1 \text{ extra } H^+ = NO_2 + H_2O$
(*b*) $(H^+, N^{5+}, 3O^{--}) + 2\ominus + 2 \text{ extra } H^+ = HNO_2 + H_2O$
(*c*) $(H^+, N^{5+}, 3O^{--}) + 3\ominus + 3 \text{ extra } H^+ = NO + 2H_2O$
(*d*) $2(H^+, N^{5+}, 3O^{--}) + 2 \times 4\ominus + 2 \times 4 \text{ extra } H^+ = N_2O + 5H_2O$
(*e*) $2(H^+, N^{5+}, 3O^{--}) + 2 \times 5\ominus + 2 \times 5 \text{ extra } H^+ = N^\circ_2 + 6H_2O$
(*f*) $(H^+, N^{5+}, 3O^{--}) + 6\ominus + 6 \text{ extra } H^+ = (N^-, 3H^+, O^{--}) + 2H_2O$
(*g*) $(H^+, N^{5+}, 3O^{--}) + 8\ominus + 8 \text{ extra } H^+ = NH_3 + 3H_2O$

The equations for the reactions between nitric acid and various reducing agents will now be presented together with experiments in which these reactions take place.

(*a*) When a glowing piece of charcoal is dropped into some warm fuming nitric acid, the charcoal burns vigorously *in* the acid.

This shows that, at high temperatures, nitric acid dissociates so as to form free oxygen. This it can do only by forming N-compounds in which N has a lesser valence than 5, as shown for instance, by the equation

$$\underset{\substack{\text{N-valence}\\=5}}{2HNO_3} = H_2O + \underset{\substack{\text{N-valence}\\=4}}{2NO_2} + O$$

Since the N in HNO_3 actually does this valence changing at high temperatures, it is to be expected that it exerts this tendency even at ordinary temperatures, as assumed throughout this discussion.

The Formation of Nitric Peroxide from Nitric Acid.—When copper reacts with concentrated nitric acid, reddish-brown fumes of NO_2 will be evolved. This reaction between copper and concentrated nitric acid is evidently a combination of equation (*a*), above—

$$(H^+, N^{5+}, 3O^{--}) + 1\ominus + 1 \text{ extra } H^+ = NO_2 + H_2O$$

and of the electromotive change of copper,

$$Cu^\circ = Cu^{++} + 2\ominus$$

In order that the electrons formed from Cu° will be taken up wholly by the

HNO_3, $2HNO_3$ must change while 1 Cu° changes; hence we multiply the first equation by 2 and obtain,

$$2HNO_3 + 2\ominus + 2H^+ = 2NO_2 + 2H_2O$$

Then, taking the second equation,

$$Cu^\circ = Cu^{++} + 2\ominus$$

adding the left sides and the right sides, cancelling the electrons, and adding the extra NO_3 ions, we obtain the common form of the equation:

$$2HNO_3 + 1Cu^\circ + 2HNO_3 = 2NO_2 + 2H_2O + 1Cu(NO_3)_2$$

The Formation of Nitric Oxide from Nitric Acid. When copper reacts with ordinary dilute nitric, a colorless gas, nitric oxide, NO—will be evolved. The reaction between dilute nitric acid and copper evidently consists of equation (*c*), and the equation for the change of copper. Here, HNO_3 and Cu must change in the ratio

$$2HNO_3 : 3Cu^\circ$$

in order that the electrons formed from the Cu° may all be used up by the HNO_3. Multiplying the corresponding equations by 2 and 3, we obtain

$$2HNO_3 + 6\ominus + 6H = 2NO + 4H_2O$$
$$3Cu^\circ = 3Cu^{++} + 6\ominus$$

Adding, cancelling the electrons, and adding the "inactive" NO_3 ions, we obtain

$$2HNO_3 + 3Cu^c + 6HNO_3 = 2NO + 4H_2O + 3Cu(NO_3)_2$$

The Reduction of Nitrates to Ammonia.—Very strong reducing agents (zinc or aluminum) reduce very dilute nitric acid or nitrates to the extreme limit—ammonia. This is conveniently accomplished as follows: secure in a test-tube some finely divided aluminum, cover it with concentrated solution of caustic soda, and add a few drops of dilute nitric acid: it will take a few minutes until vigorous action sets in, then the presence of ammonia will be noticeable.

The equation for this reaction is the sum of equation (*g*) above, and of the equation for the electromotive change of aluminum. From the numbers of electrons involved in these changes, it is evident that $3HNO_3$ change while 8Al change. Hence we multiply the first equation by 3,

$$3HNO_3 + 3 \times 8\ominus + 3 \times 8 \text{ extra } H^+ = 3NH_3 + 9H_2O$$

and the second by 8, thus:

$$8Al = 8Al^{+++} + 24\ominus$$

On adding these, we obtain

$$3HNO_3 + 8Al + 24 \text{ extra } H^+ = 3NH_3 + 9H_2O + 8Al^{+++}$$

To get the final equation, we must add extra ions to change $8Al^{+++}$ to $8NaAlO_2$. This requires $8Na^+$ ions, and $16O^{--}$ ions. These and also the 24 extra H^+ ions in the equation above will be supplied if we add 8NaOH and $8H_2O$. Hence adding 8NaOH and $8H_2O$ in place of the 24 extra H^+, and putting $8NaAlO_2$ in place of $8Al^{+++}$, we obtain the final form

$$3HNO_3 + 8Al + 8NaOH + 8H_2O = 3NH_3 + 8NaAlO_2 + 9H_2O$$

In its simplest form, this equation is evidently,

$$3NaNO_3 + 8Al + 5\ NaOH + 2H_2O = 3NH_3 + 8NaAlO_2$$

Other Examples of the Oxidizing Actions of Nitric Acid.—(*a*) Action upon insoluble sulphides—*e.g.*, CuS, Bi_2S_3, Ag_2S. These sulphides generally change to the ordinary cations and free sulphur, hence their oxidation is expressed by the following equations:

$$CuS = Cu^{++} + 2\ominus + S^\circ$$
$$Bi_2S_3 = 2Bi^{+++} + 6\ominus + 3S^\circ$$
$$Ag_2S = 2Ag^{+} + 2\ominus + S^\circ$$

It is useless to try to decide whether both components of the sulphide have a *zero* valence, and hence the metal is oxidized, or that the metals have their positive valences, and the sulphur its negative valence (*e.g.*, $Cu,^{++}$, S^{--}) and that the latter is changed from 2^- to 0: either idea may be used.

The reduction product of nitric acid acting upon metal sulphides depends upon the concentration of the acid: with ordinary dilute acid, NO is formed; hence the change of the nitric acid is

$$(H^+,\ N^{+5},\ 3O^{--}) + 3\ominus + 3H^+ = NO + 2H_2O$$

Hence, for CuS, $2HNO_3$ react with 3CuS because 3CuS produce $6\ominus$ and this is enough for $2HNO_3$. Adding the corresponding equations—multiplied by 3 and 2 respectively—and inserting the inactive NO_3^- ions, we obtain

$$3CuS + 2HNO_3 + 6HNO_3 = 3Cu(NO_3)_2 + 3S + 2NO + 4H_2O$$

With Bi_2S_3, we obtain in the same manner

$$Bi_2S_3 + 2HNO_3 + 6HNO_3 = 2Bi(NO_3)_3 + 3S + 2NO + 4H_2O$$

With Ag_2S, we obtain

$$3Ag_2S + 2HNO_3 + 6HNO_3 = 6AgNO_3 + 3S + 2NO + 4H_2O.$$

(*b*) Action of "Aqua Regia."—A mixture of one volume concentrated nitric with three volumes of concentrated hydrochloric acid is employed to dissolve metals (gold, platinum) and to act upon metal sulphides which are not acted upon by nitric acid (HgS). In this mixture, the nitric acid is relatively dilute—diluted by the hydrochloric acid—but the high H^+ concentration in the mixture helps the nitric acid to exert a high oxidation potential. A part of the oxidizer is always wasted in the formation of free chlorine, but this action is not rapid because the chlorine is held for a while in the form of several unstable compounds such as nitrosyl chloride (NOCl), hypochlorous acid (HOCl). However, in the end all the chlorine produced by the "wasted" oxidizing action appears as Cl_2[1] and practically all the nitrogen escapes as NO. Hence chlorine is formed according to the following equations:

$$(H^+,\ N^{5+},\ 3O^{--}) + 3\ominus + 3H^+ = NO + 2H_2O$$
$$2(H^+,\ Cl^-) = Cl_2^\circ + 2H^+ + 2\ominus$$

To make the number of electrons formed by the change of HCl equal to the number used up by HNO_3, we must multiply the first equation by 2 and the last by 3. Adding the resulting equations, and cancelling the $6H^+$ and $6\ominus$ from both sides, we obtain

$$2HNO_3 + 6HCl = 3Cl_2^\circ + 2NO + 4H_2O$$

[1] HNO_3 can oxidize chloride ion only when the latter is sufficiently concentrated to raise the potential of its change *above* that of HNO_3 in our Table, *q.v.*, Nos. 29 and 31.

The portion of the oxidizer (HNO_3) that spends itself upon another substance put into the *aqua regia* (HgS, Au, Pt, etc.) naturally does not form free chlorine as an end result, and hence is best considered as acting directly with the substance treated. Since the oxidizing power of the nitric acid is the only one acting in *aqua regia*, it follows that the oxidizing power of this mixture cannot be (is not) greater than that of the nitric acid; and hence the question arises: why is nitric acid alone unable to act upon such substances as HgS, Au, or Pt? The answer is: the chlorides of these metals are only slightly ionized, and very few free Hg^{++} or Au^{+++}, or Pt^{++++} ions remain to oppose the formation of more of the latter; whereas, in the absence of Cl^- ion, the first (even small) portions formed, of Hg^{++}, etc., remain as free ions, and stop further action.

Hence the portion of *aqua regia* which acts direct upon HgS acts in accordance with the following equations (derived by means of *method* 2 for writing such equations —see Part I):

$$HgS + 2HCl = HgCl_2 + S^\circ + 2H^+ + 2\ominus$$
$$HNO_3 + 3H^+ + 3\ominus = NO + 2H_2O$$

Multiplying the first by 3 and the second by 2, adding the resulting equations, and simplifying, we obtain

$$3HgS + 6HCl + 2HNO_3 = 3HgCl_2 + 3S^\circ + 2NO + 4H_2O$$

The action upon gold takes place according to the equations

$$Au^\circ + 3Cl^- = AuCl_3 + 3\ominus$$
$$HNO_3 + 3H^+ + 3\ominus = NO + 2H_2O$$

Adding, we obtain

$$Au + 3HCl + HNO_3 = AuCl_3 + NO + 2H_2O$$

(c) The action of concentrated nitric acid upon some non-metals such as sulphur, phosphorus, etc., results in the formation of the highest oxidation product of these non-metals and of the reduction of HNO_3 to NO_2. Thus, with sulphur the equations are

$$(H^+, N^{5+}, 3O^{--}) + 1\ominus + H^+ = NO_2 + H_2O$$
$$S^\circ + 4(O^{--} + 2H^+) = (2H^+, S^{6+}, 4O^{--}) + 6\ominus + 6H^+$$

Multiplying the first by 6, and adding the result to the last equation, we obtain—after cancelling the $6\ominus$, $4H_2O$ and $6H^+$ from both sides

$$6HNO_3 + S^\circ = 6NO_2 + H_2SO_4 + 2H_2O$$

Nitrous Acid and Nitrites.—Although the nitrogen in nitrites is in a lower state of oxidation than that in nitrates, and their potential as oxidizing agents less than that of nitrates, yet they react more readily than nitrates, and hence they *appear* to be stronger oxidizing agents. However, they are really weaker. The potential of the change from HNO_2 to lower reduction products is 1.2 to 1.3 volts or HNO_2 is 0.5 to 0.3 volt weaker as an oxidizing agent than HNO_3,.

Reduction products formed from nitrous acid or nitrites are practically identical with those of nitric acid, and hence the equations for the reduction of nitrous acid need not be presented.

Strong oxidizing agents (acidified permanganate), oxidize nitrous acid to nitric acid. The action is quantitative and hence is employed to estimate the amount of nitrites in a sample. The equation for this change is obtained as follows: nitrogen in HNO_2 has 3^+ charges,—that in HNO_3, 5^+, and the latter also contains one O more, which is obtained from the solution in the form of an ion, O^{--}, from water. Hence this change is expressed as follows:

$$(H^+, N^{3+}, 2O^{--}) + (2H^+, O^{--}) = (H^+ + N^{5+}, 3O^{--}) + 2\ominus + 2H^+$$

The change undergone by the permanganate is explained under the corresponding heading below, and given here without comment:

$$2(K^+, Mn^{7+}, 4O^{--}) + 10\ominus + 8(2H^+, SO_4^{--}) = K_2SO_4 + 2MnSO_4 + 8H_2O + 5SO_4^{--}$$

To make the number of electrons produced by the change of the nitrous acid equal to that taken up by the permanganate, we must multiply the first equation by 5; then adding them we obtain:

$$5HNO_2 + 2KMnO_4 + 5H_2O + 8H_2SO_4 = 5HNO_3 + K_2SO_4 + 2MnSO_4 + 8H_2O + 5H_2SO_4$$

This equation can be simplified by taking out $5H_2O$ and $5H_2SO_4$ from both sides.

Hydroxylamine.—This is a very active reducing agent of the composition NH_2OH. It forms salts with acids just as ammonia does, but it is a much weaker base than ammonia. Hydroxylamine is produced by the reduction of nitric acid: when the reduction is not properly regulated, other reduction products—notably NH_3—are formed. The reduction is most easily effected electrolytically: with proper current densities and a mercury cathode, nitric acid in dilute H_2SO_4 is reduced almost quantitatively to hydroxylamine sulphate. The equation for this reduction is:

$$(H^+, N^{5+}, 3O^{--}) + 6\ominus + 6H^+ = (N^-, 3H^+, O^{--}) + 2H_2O$$

On evaporation, the cathode liquid will give crystals of hydroxylamine sulphate $2NH_2OH.H_2SO_4$.

Hydroxylamine is a splendid reducing agent. According to the vigor of the oxidizing agent with which it reacts, its nitrogen will be oxidized to any of the following stages: N_2°, N^+, N^{+++}, etc. Thus with Fehling's solution, it will change quantitatively to N_2O. Fehling's solution contains cupric ion, Cu^{++}, and this is reduced to cuprous ion, Cu^+ (*i.e.*, Cu_2O), according to the equation:

$$2Cu^{++}(OH)_2^- + 2\ominus = Cu_2O + H_2O + 2OH^-$$

The elemental ions of hydroxylamine are, $(N^-, 3H^+, O^{--})$, hence the nitrogen changes from 1^- to 1^+ according to the equation:

$$2(N^-, 3H^+, O^{--}) = N_2O + 4\ominus + H_2O + 4H^+$$

To make the electrons produced equal to those used up, we must multiply the former equation by 2. Then adding the result to the last equation above, we obtain:

$$4Cu(OH)_2 + 2(NH_2OH) = 2Cu_2O + 7H_2O + N_2O$$

When hydroxylamine salt is put into excess of acidified permanganate solution, the nitrogen is oxidized almost quantitatively to NO_2, the action taking place according to the following equations:

$$(N^-, 3H^+, O^{--}) + (2H^+, O^{--}) = (N^{4+}, 2O^{--})_4 + 5\ominus + 5H^+$$
$$(K^+, Mn^{7+}, 4O^{--}) + 5\ominus + 8H^+ = K^+ + Mn^{++} + 4H_2O$$

Adding these equations, dropping $4H^+$ and one H_2O from both sides, and inserting the inactive anions, $2SO_4^{--}$ on both sides, we obtain

$$(NH_2OH) + KMnO_4 + 2H_2SO_4 = NO_2 + KHSO_4 + MnSO_4 + 3H_2O$$

The extent to which hydroxylamine may be oxidized by other oxidizing agents may be inferred by noting the position in the Table of such oxidizing agents, and recalling the above actions of acidified permanganate (line 32) and of cupric salts (line 21—the potential of Cu^{++} changing to Cu^{+} being practically identical with that of Cu^{++} changing to Cu°).

Hydrazine.—This substance has the formula N_2H_4, and it forms salts of the formula $N_2H_4.HCl$. Its elemental ions are evidently $(2N^{--}, 4H^{+})$. It is a strong reducing agent: a solution of the free base is oxidized by the oxygen of the air even. It reduces silver oxide to silver, cupric to cuprous, etc., and even free sulphur to H_2S. Its oxidation product is almost always N_2; and this action naturally takes place according to the equation:

$$(2N^{--}, 4H^{+}) = N_2^{\circ} + 4H^{+} + 4\ominus$$

Since the nitrogen in hydrazine is in a higher oxidation stage than that in ammonia hydrazine can also be reduced to NH_3, and even when it is oxidized by such a strong oxidizing agent as acidified permanganate, a part of the hydrazine is reduced to ammonia.

The fact that most—or all—of the "hydrazine nitrogen" is oxidized to N_2° is undoubtedly due to the fact that the two N's in hydrazine are directly connected. It is on account of the presence of the 2N nucleus that hydrazine is not formed from nitric acid or other 1N compounds by reduction, but is obtained by reducing hyponitrous acid, $(HON)_2$.

Other compounds of nitrogen, such as hydrazoic acid, diazo compounds, etc., are not used ordinarily in oxidation-reduction reactions and hence need not be considered here.

Ammonia and Its Salts.—Although these compounds contain nitrogen in the *lowest* state of oxidation, they are not correspondingly *active* reducing agents:[1] they are oxidized only by strong oxidizing agents, or under special conditions. With free chlorine, the nitrogen in ammonium salts will change to free nitrogen or N^{+++} (*i.e.*, NCl_3) according to the following equations:

$$2(N^{3-}, 4H^{+}, Cl^{-}) = N_2^{\circ} + 8H^{+} + 2Cl^{-} + 6\ominus$$
$$(N^{3-}, 4H^{+}, Cl^{-}) = N^{+++} + 4H^{+} + Cl^{-} + 6\ominus$$

The equation for the reduction of the chlorine is

$$Cl_2^{\circ} + 2\ominus = 2Cl^{-}$$

Multiplying the latter by 3, and adding the result to each of the preceding equations in turn, we obtain

$$2NH_4Cl + 3Cl_2 = N_2 + 8HCl$$
$$NH_4Cl + 3Cl_2 = NCl_3 + 4HCl$$

With bromine, which is a weaker oxidizing agent than chlorine, the oxidation of the nitrogen stops mainly at the zero valence—that is, free nitrogen is produced. With iodine, the action on acidified solutions of ammonium salts is negligible. In neutral or *alkaline* solutions, the tendency of ammonia to be oxidized is much greater than in acid solutions because these reactions involve the formation of free H^{+} ion (see equations above), and a lesser H^{+} ion concentration will increase the potential

[1] Attention has been called to this in the general discussion in Part I and a reason given for this anomaly.

of this reaction of the reducer. This more than offsets the corresponding change in the potential of the oxidizing halogen. The latter changes from free halogen to hypohalite, and these are weaker oxidizing agents in alkaline solutions than the free halogens from which they are formed (see under "Halogens"). However, the amount by which the potential of the oxidizing agent is thus lessened is evidently more than offset by the before-mentioned increase in the reaction tendency of the ammonia, so that we find even iodine oxidizing free ammonia vigorously, to NI_3. The latter crystallizes with one molecule of NH_3, which gives the compound the formula $NH_3 \cdot NI_3$.

Nitric acid does not oxidize ammonium salts appreciably at ordinary temperatures, but the rapidity of the action increases with rise of temperature, and is appreciable in boiling solutions. At slightly higher temperatures, mixtures of ammonium salts with nitrates react rapidly. The nitrogen from both is changed to the N^+ form, *i.e.*, N_2O is formed—according to the equation

$$(N^{3-}, 4H^+, Cl^-) + (Na^+, N^{5+}, 3O^{--}) = N_2O + 2H_2O + NaCl.$$

Nitrites—which react more readily than nitrates—oxidize ammonium salts rapidly even at temperatures slightly below 100°. Thus on boiling a solution containing $NaNO_2$ and NH_4Cl, the following reaction takes place:

$$(Na^+, N^{3-}, 2O^{--}) + (N^{3-}, 4H^+, Cl^-) = NaCl + N_2^\circ + 2H_2O$$

At ordinary temperatures, acidified permanganate and bichromate solutions do not oxidize ammonium salts extensively, but at higher temperatures, *e.g.*, in hot solutions, the action takes place quite rapidly and results in the formation of nitrogen. This also takes place in alkaline solutions, although here these oxidizing agents have necessarily a much smaller tendency to be reduced: this is more than offset by the larger tendency of ammonia to be oxidized.

At ordinary temperatures, ammonia gas and oxygen do not react; but at higher temperatures, *i.e.*, when they are heated from an external source of heat, ammonia may be ignited and will burn to form nitrogen and water. When the hot gases come in contact with platinum, nitric oxide is formed (principle of commercial production of nitric acid from ammonia).

Phosphorus, Arsenic, Antimony, and Bismuth.—The total range of oxidation stages of these elements is the same as that for nitrogen: it extends from the state corresponding to nitric acid (E^{5+}) to the stage corresponding to ammonia (E^{3-}) except in the case of bismuth in which the free element is the lowest oxidation stage known.

In its highest oxidation stage, phosphorus exerts absolutely no oxidizing tendency, in other words, phosphoric acid is not reducible in aqueous solutions. Concerning the other metals of this group, it may be said that the oxidizing tendency—or reducibility—of their highest oxidation stages increases with increasing atomic weight, so that the highest oxide of bismuth is a fairly strong oxidizing agent.[1] Correspondingly the lower oxidation stages show less tendencies to pass to the higher stages—or, in other words, the lower oxidation stages of phosphorus are stronger reducing agents than those of arsenic, and those of arsenic less than those of antimony. There is no appreciable difference between bismuth and antimony, so that the electromotive force required for the electrolytic deposition of these metals out of solutions of their chlorides are practically the same, and near that of copper (see Table, Nos. 18 and 21). None of the compounds of these elements are used as oxidizing agents except the so-called "bismuth peroxide."[1]

[1] The formula of such a compound is not definitely known beyond the fact that it contains bismuth with a valence greater than *three*.

However, the reduction of $Bi(OH)_3$ to black BiO by means of an alkaline solution of Na_2SnO_2 serves as a delicate test for bismuth, hence its reaction is given here.

$$2Bi(OH)_3 + 2\ominus = 2BiO + 3H_2O + O^{--}\quad Na_2SnO_2 + O^{--} = Na_2SnO_3 + 2\ominus$$

or, together:

$$2Bi(OH)_3 + Na_2SnO_2 = 2BiO + 3H_2O + Na_2SnO_3.$$

Hypophosphites, phosphites, and arsenites are used occasionally as reducing agents. Hypophosphites are strong reducing agents. They reduce concentrated sulphuric acid to SO_2 or to free sulphur, cupric ion (*e.g.*, from $CuSO_4$) to copper hydride, silver ion (from $AgNO_3$) to silver, etc. They are derived from the free acid, H_3PO_2, the elemental ions of which are ($3H^+$, P^+, $2O^{--}$). Its salts are readily prepared by the action of yellow phosphorus on warm aqueous solutions of strong bases. In this case a part of the phosphorus changes to phosphine (reduction!) while another part changes to hypophosphite. The latter is a mono-basic acid ion of the formula $H\,PO{\cdot}OH^-$. It contains phosphorus with a polar valence of 1^+ because its elemental ions are ($2H^+$, P^+, $2O^{--}$) the electric charges of which give an algebraic sum of 1^- and this belongs to the *ion as a whole*. Its formation evidently takes place according to the equation

$$P + H_2O + O^{--} = (H_2PO_2)^- + 1\ominus$$

while the reduction to PH_3 takes place according to the equation

$$P + 3HOH + 3\ominus = PH_3 + 3OH^-$$

The relation of the forces which brings about this reaction were discussed in the latter part of Part I under the heading "Substances Which Act Simultaneously as Oxidizers and as Reducers."

Phosphites are determined quantitatively by titration with iodine in neutral or in acid solutions. Alkaline solutions cannot be used because in such solutions iodine will change to iodide and hypoiodite, and the latter will rapidly change further—to iodate (see below under "Halogens") and thus the quantitative relation between iodine and the other reacting substance would be disturbed. Iodine reacts with H_3PO_3 as follows:

$$(3H^+,\ P^{+++},\ 3O^{--}) + H_2O = H_3PO_4 + 2H^+ + 2\ominus$$
$$I_2^\circ + 2\ominus = 2I^-$$

Hence,

$$H_3PO_3 + H_2O + I_2 = H_3PO_4 + 2HI$$

All oxidizing actions lower in our Table than the iodide-iodine reaction will naturally also oxidize phosphites.

Arsenites and other trivalent arsenic compounds ($AsCl_3$, As_2O_3, etc.) also may be determined quantitatively by oxidation with iodine.

However, the titration of arsenic trioxide with iodine is quantitative only when carried out in faintly acid solutions. The reason why the solution must be *faintly* acidified during the change is this: the oxidation of the arsenic involves H^+ ion as is shown by the following equation:

$$Na_3AsO_3 + H_2O = Na_3AsO_4 + 2H^+ + 2\ominus$$

and hence its potential decreases with increase in H^+ ion concentration. But the change of the iodine does not involve—is independent of—the H^+ ion concentration. Hence with increasing H^+ ion concentration, the difference between the two potentials decreases and soon becomes zero, and then there is no force to impel the reaction. With H_3PO_3—which is a stronger reducing agent than arsenious acid—a moderate concentration of H^+ ion still leaves the potential of "phosphorous acid changing to phosphoric acid" large enough to act with iodine.

Arsenic trioxide is used frequently to reduce nitric acid to nitric peroxide, NO_2—*i.e.*, to reduce HNO_3 to the least extent possible: hence this extremely weak reducing agent is chosen. This reaction takes place according to the following equations:

$$(2As^{+++},\ 3O^{--}) + 6H^+ + 5O^{--} = 2(3H^+,\ As^{5+},\ 4O^{--}) + 4\ominus$$
$$(4H^+,\ N^{5+},\ 3O^{--}) + 4\ominus + 4H^+ = 4NO_2 + 4H_2O$$

On addition, we obtain

$$As_2O_3 + 4HNO_3 + 5H_2O = 2H_3AsO_4 + 4NO_2 + 4H_2O.$$

The production of arsine (AsH_3) and of stibine (SbH_3) by reduction—from higher oxidation stages of arsenic or antimony respectively—can be accomplished in acid solutions by means of zinc, iron, etc. The equations for the change with zinc are given here

$$Zn^\circ = Zn^{++} + 2\ominus$$
$$As^{+++}Cl_3^- + 6\ominus + 3H^+ = As^{3-}H_3^+ + 3Cl^-$$

Multiplying the first by 3, inserting on both sides the $3Cl^-$ to accompany the 3^+H in the second, and adding the resulting equations, we obtain

$$3Zn + AsCl_3 + 3HCl = AsH_3 + 3ZnCl_2$$

Oxygen.—This element can exist in three distinct oxidation stages, which in their order from lowest to highest stage, are: (1) oxygen as a constituent of all ordinary oxides, O^{--}; (2) as a constituent of true peroxides, *e.g.*, hydrogen peroxide, H_2O_2, barium peroxide, BaO_2, etc., in which the polar valence of oxygen is 1^-; and (3) as the free element, O_2° or O_3° (ozone). Thus peroxides appear as containing oxygen which has been *reduced* from the free element *half-way* to the lowest possible state of oxidation, and this view of the state of the oxygen in peroxides is in accord with its properties: it can act in either capacity—as an oxidizer, changing itself to O^{--}, or as a reducer, changing itself to O_2°.

Mathematically we could consider peroxides to be compounds formed by the addition of free oxygen to ordinary oxides, which at the time of action dissociate into these constituents. But this view does not suggest the behavior of peroxides as reducing agents, and hence is inferior to the other view.

In aqueous solution, the oxygen ion, O^{--}, exists *as such only* in extremely small amounts; but it is always in equilibrium with its hydrated form, OH^-, through the equation

$$O^{--} + H_2O = 2OH^-$$

and the OH^- concentration is known through the acidity or alkalinity of the solution.

Since the concentration of H_2O in all ordinary aqueous solutions is practically the same, the mass-law gives us the following relation between the materials in the above equation "at equilibrium."

$$[O^{--}] \times [H_2O\ \text{Const.}] = (\text{Const.}) \times [OH^-]^2$$

or

$$\frac{[O^{--}]}{[OH^-]^2} = (\text{Const.})$$

that is, the ratio of the concentration of O^{--} to the square of the OH^- concentration is constant—or the variations in O^{--} concentration are proportional to the square root of the variations in the OH^- concentration. The OH^- concentrations—in turn—are known to vary as the *reciprocal* of the H^+ concentrations, because $H^+ + OH^-$

$= H_2O$, and according to the mass law—$[H^+] \times [OH^-] = (\text{Const.})$. With these facts and the further fact that elementary oxygen has a slight, but roughly constant solubility in all aqueous solutions, we can consider the tendency of the various forms of oxygen to change to free oxygen, O_2.

From the foregoing, it is evident that the tendency of O^{--} to change to O_2° is greatest with a high concentration of OH^-, intermediate in neutral solutions, and lowest in strongly acidified solutions. Number 26 in the table corresponds to the second, *i.e.*, neutral solutions, Or conversely, the tendency of O_2° to change to O^{--} (or OH^-) is greatest in acid solutions, and least in alkaline solutions. Hence, we may say that oxygen gas will react with (oxidize) any of the substances in the left column of the table above line 26, and that this will be particularly the case if the solution is acidified (small OH^+ concentration). With silver and mercury, the forces impelling the combined changes (differences between the numbers in the central column) are small, and hence the actions take place slowly; but with substances farther up in the table, the actions are correspondingly more rapid. In all such cases, the actions may be inferred from the table because the substances in the left-hand column change to the substances on the same line in the right-hand column, while oxygen—which is in the right-hand column on a line below No. 26 —changes to OH^- which either remains as such or combines with H^+ to form H_2O. Some examples follow.

(*a*) An aqueous solution of hydrogen sulphide exposed to the air undergoes the following changes:

$$2S^{--} = 2S^\circ + 4\ominus \text{ (see table, line 11)}$$
$$O_2^\circ + 4\ominus = 2O^-$$

Adding and inserting the four H^+ coupled with $2S^{--}$, we obtain

$$2H_2S + O_2 = 2H_2O + 2S$$

(*b*) An acidified solution of $FeSO_4$ exposed to the air undergoes the following reaction:

$$4Fe^{++} = Fe^{+++} + 4\ominus$$
$$4H^+ + O_2^\circ + 4\ominus = 2H_2O$$

Adding and inserting the inactive $6SO_4^{--}$, we obtain

$$4FeSO_4 + 2H_2SO_4 + O_2 = 2Fe_2(SO_4)_3 + 2H_2O$$

(*c*) A piece of copper projecting into a dilute acid will undergo the following reactions, particularly at the points where it projects into the air.

$$2Cu^\circ = 2Cu^{++} + 4\ominus$$
$$4H^+ + O_2 + 4\ominus = 2H_2O$$

Adding, and inserting the inactive anions of the acid, we obtain

$$2Cu + 4HCl + O_2^\circ = 2CuCl_2 + 2H_2O$$

Since the oxygen in peroxides is in a state intermediate between that of the free element and of the bivalent anion O^{--}, it has two distinct tendencies to change, namely, either to be oxidized to O_2° or to be reduced to O^{--}. Either one of these can take place in alkaline, or in acid solutions—the corresponding equations and potentials are here given for $N/1$ NaOH and $N/1H_2SO_4$ respectively.

Oxidation of the peroxide in alkaline solutions—potential, 2.02 volts

$$(2Na^+, 2O^-) + 2OH^- = O_2^\circ + 2\ominus + 2NaOH$$

Under these conditions it is a reducing agent equal in effect to tin in neutral or acid solutions.

Oxidation of peroxide in acid solutions—potential, 1.20 volts

$$(2H^+, 2O^-) = O_2^\circ + 2\ominus + 2H^+$$

Under these conditions it is only a feeble reducing agent, equal to ferrous salts changing to ferric.

Reduction of the peroxide in alkaline solutions—potential, 1.16 volts

$$(2Na^+, 2O^-) + 2\ominus + 2H_2O = 4(OH)^- + 2Na^+$$

Under these conditions it is feeble oxidizing agent.

Reduction of peroxide in acid solutions—potential 0.34 volt

$$(2H^+, 2O^-) + 2\ominus + 2H^+ = 2H_2O$$

Under these conditions it is a fairly strong oxidizing agent.

Peroxide in alkaline solutions reduces silver oxide (Ag^+) to silver metal—a reaction which is to be expected from the potential relations. The equations for this change are

$$(2Na^+, 2O^-) + 2(OH)^- = O_2^\circ + 2\ominus + 2NaOH$$
$$2Ag^+, O^{--} + 2\ominus + H_2O = 2Ag^\circ + 2(OH)^-$$

Adding these and cancelling the $2\ominus$ and the $2(OH)^-$ common to both sides, we obtain:

$$Na_2O_2 + Ag_2O + H_2O = O_2 + 2NaOH + 2Ag$$

In acidified solutions, H_2O_2 is oxidizable by strong oxidizing agents, such as acidified permanganate, acidified bichromate, free chlorine, free bromine, and concentrated nitric acid, or in other words, by the substances in the right column of the table *below line* 24. Since its reaction with acidified permanganate is frequently employed for the quantitative determination of H_2O_2, the equations for it will be given here. The equation for the peroxide is as derived above, and that for the acidified permanganate is derived under "Manganese."

$$5(2H^+, 2O^-) = 5O_2^\circ + 10\ominus + 10H^+$$
$$2(K^+, Mn^{7+}, 4O^{--}) + 16H^+ + 10\ominus = 2K^+ + 2Mn^{++} + 8H_2O$$

Adding, cancelling the $10H^+$ and $10\ominus$ common to both sides, and adding $3SO_4^{--}$ to both sides, we obtain

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = 5O_2^\circ + K_2SO_4 + 2MnSO_4 + 8H_2O$$

In concluding this section on oxygen, a few words should be said about ozone. This is a very strong oxidizing agent, or very active form of oxygen, but in its action only 1O out of the molecule O_3 is reduced to O^{--}—the other two oxygen atoms are obtained as O_2°. Ozone reacts quantitatively with H_2O_2 in accordance with the following equations:

$$O_2O^\circ + 2\ominus + H_2O = O_2 + 2(OH)^-$$
$$(2H^+, 2O^-) = O_2^\circ + 2\ominus + 2H^+$$

Adding these equations we obtain

$$O_3 + H_2O + H_2O_2 = 2O_2 + 2H_2O$$

Sulphur.—This element, similar to nitrogen, exists in a number of oxidation stages, the lowest of which is the *sulphide* stage, and the highest, the persulphate stage, $H_2S_2O_8$ or $Na_2S_2O_8$. These different stages and the relations between them are shown in the following table.

COMPOUNDS OF SULPHUR IN ASCENDING ORDER OF OXIDATION STAGES

Order	Common form of each oxidation stage	Theoretical elemental ions	Oxidation electrons per S
1	Hydrogen Sulphide (and other Sulphides)	$2H^+$, S	0
2	Sulphur	S°	2
3	Hyposulphurous Acid ($H_2S_2O_4$) (*Not* Thio-sulphuric Acid.)	$2H^+, 2S^{3+}, 4O^{--}$	5
4	Sulphur Dioxide (Sulphurous Acid, Sulphites)	S^{4+}, $2O^{--}$	6
5	Sulphuric Acid (Sulphates)	$2H^+$, S^{6+} $4O^{--}$	8
6	Persulphuric Acid (Persulphates)	$2H^+, 2S^{7+}, 8O^{--}$	9

In addition to the oxidizing stages in this table there are a number of oxidation stages such as thiosulphate and the various thionates, which are not formed in the ordinary oxidation-reduction changes of sulphur compounds.

Persulphates are strong oxidizing agents, which change to sulphates on reduction. Concentrated sulphuric is a strong oxidizing agent which gives different reduction products according to the strength of the reducing agent. Sulphur dioxide acts as an *oxidizing* agent to strong reducing agents, but it acts as a mild *reducing* agent toward oxidizing agents. All lower oxidation stages of sulphur act as reducing agents only. The strongest of these is the hyposulphite. Sulphur and sulphides are only feeble reducing agents—partly because they are slightly soluble in water and hence can be in solution only in small concentrations.

Persulphuric acid is prepared by anodic oxidation of concentrated sulphuric acid—the change at the anode takes place according to the equation

$$2(HSO_4)^- = H_2S_2O_8 + 2\ominus$$

The action consists of the discharge of electrons from the HSO_4^- ion, and the union of two such radicals. It is a powerful oxidizing agent even in alkaline solutions.

Sulphuric acid is an oxidizing agent only in the concentrated form. Its oxidizing power is then approximately the same as nitric acid, and like the latter is used to dissolve silver, copper, etc. It does not attack gold or platinum. Weak reducing agents, such as silver or copper, reduce it to the next lower oxidation stage—SO_2. Strong reducing agents such as zinc, iodides, etc., reduce it to a much lower stage *i.e.*, sulphur, or H_2S even.

The following equations express the reduction of H_2SO_4 to its reduction products:

$$(a)\ H_2SO_4 + 2\ominus + 2H^+ = SO_2 + 2H_2O$$
$$(b,\ H_2SO_4 + 6\ominus + 6H^+ = S + 4H_2O$$
$$(c)\ H_2SO_4 + 8\ominus + 8H^+ = H_2S + 4H_2O$$

The equation for the reaction between copper and sulphuric acid is obtained by adding equation (*a*) above to the equation for the change of copper because 1 Cu produces as many electrons, *i.e.*, 2—as $1H_2SO_4$ uses up to form SO_2. The addition of these equations gives

$$Cu + H_2SO_4 + 2H^+ = Cu^{++} + SO_2 + 2H_2O$$

Adding the inactive SO_4^{--} ions, we obtain

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$$

To obtain the equation for the reaction between Zn and H_2SO_4, add together equation (a) above and

$$4Zn = 4Zn^{++} + 8\ominus$$

The fact that stronger reducing agents reduce such oxidizing agents as concentrated sulphuric acid to a greater extent than weaker reducing agents is shown well by the action between concentrated sulphuric acid and chlorides, bromides, and iodides respectively It is evident from the position of the latter in the table of Oxidation Changes that their tendency to form the free halogens increases in the order in which they are here named—chlorides, bromides, iodides—and in accordance with this we find that in the action of concentrated sulphuric acid with chlorides there is no oxidation or reduction, with bromides there is formation of bromine and slight reduction of the sulphuric acid (to SO_2), while with iodides there is formation of iodine and very extensive reduction of the sulphuric acid (to sulphur, or to hydrogen sulphide even). With bromides, the reactions are

$$2NaBr = 2Na^+ + Br_2^\circ + 2\ominus$$

Adding this to No. (*a*) above, and inserting $1SO_4^{--}$ ion on both sides, we obtain

$$2NaBr + 2H_2SO_4 = Na_2SO_4 + SO_2 + 2H_2O + Br_2$$

With iodides, the reactions are

$$2NaI = 2Na^+ + I_2^\circ + 2\ominus$$

Multiplying this by 3 (or by 4) and adding No. (*b*) (or No. (*c*)) above, we obtain the final equation.

A mixture of sulphur and concentrated sulphuric acid will react to form SO_2—the S° being oxidized and the H_2SO_4 reduced correspondingly.

Sulphur dioxide and sulphites are oxidized quantitatively to sulphuric acid (or sulphates) by means of iodine in neutral or acidified solutions. Alkaline solutions cannot be employed because in these iodine reacts in another manner (to form iodide and hypoiodite) and this reaction destroys the quantitative relation. In neutral or acid solutions, the reactions are

$$Na_2SO_3 + H_2O = Na_2SO_4 + 2H^+ + 2\ominus$$
$$I_2^\circ + 2\ominus = 2I^-$$

On addition we obtain

$$Na_2SO_3 + H_2O + I_2^\circ = Na_2SO_4 + 2HI$$

Since the formation of HI would result in the liberation and loss of SO_2, some $NaHCO_3$ is added to the solution. Since, furthermore, the action between iodine and sulphites induces a direct action of air (oxygen) on the sulphite, a trace of alcohol, glycerin, or sugar is added to the mixture; this acts as a negative catalyzer upon the latter reaction. All oxidizing changes which appear lower in our Table than the "iodide-iodine reaction" will naturally oxidize SO_2 and its compounds.

Sulphur dioxide oxidizes hydrogen sulphide both in the gaseous phase, and in aqueous solution. The sulphur from both forms will be changed to free sulphur. This reaction has produced many sulphur deposits in the earth. In this action, H_2S is oxidized according to the reaction

$$H_2S = S^\circ + 2H^+ + 2\ominus$$

while SO_2 is reduced thus,

$$SO_2 + 4\ominus = S^\circ + 2O^{--}$$

and the combined action is

$$2H_2S + SO_2 = 3S^\circ + 2H_2O$$

When this reaction takes place in aqueous solution, some pentathionic acid, $H_2S_5O_6$, is also formed, according to the equation

$$10H_2SO_3 + 4H_2S = 3H_2S_5O_6 + 12H_2O$$

Hyposulphites (not thiosulphates!) are very strong reducing agents. The most familiar of these is the zinc salt which is obtained by dissolving zinc in aqueous sulphurous acid—it dissolves without the evolution of hydrogen, and forms a yellow solution of ZnS_2O_4. The reactions are the following:

$$Zn^\circ = Zn^{++} + 2\ominus$$
$$2(2H^+, S^{4+}, 3O^{--}) + 2\ominus = (S_2O_4)^{--} + 2H_2O$$
$$Zn + 2H_2SO_3 = ZnS_2O_4 + 2H_2O$$

According to the strength of the oxidizing agent reacting with them, hyposulphites change to sulphites or sulphates.

Free sulphur acts as an *oxidizing* agent in a number of examples in which its addition to a compound corresponds to the addition of an atom of oxygen. Thus in the preparation of "yellow" ammonium sulphide, sulphur is merely added to, and readily taken up by, ammonium sulphide solution, according to the equation

$$(NH_4)_2S + xS = (NH_4)_2SS_x$$

The highest value that x can have is 4—which corresponds to the 4 oxygen atoms in $(NH_4)_2SO_4$. It is logical to assume that the sulphur thus taken up is bivalent—just as the corresponding oxygen is assumed to be bivalent. However, this sulphur is so readily separated again from this compound that the latter acts as though it contained free sulphur merely. Hence when stannous sulphide, antimony trisulphide, or arsenious sulphide are treated with yellow ammonium sulphide, they are changed to stannic sulphide, antimony pentasulphide, or arsenic sulphide respectively —*i.e.*, they are changed to a higher valence. Sulphur also combines directly with sulphites in neutral solutions to form thiosulphate, according to the equation

$$Na_2SO_3 + S = Na_2S_2O_3$$

The sulphur seems to add itself in the same manner as the fourth atom of oxygen required for the sulphate.

Thiosulphates have an appreciable tendency to dissociate into sulphite and sulphur, *i.e.*, the above reaction is reversible. Hence, when its solution is boiled with copper filings, we obtain CuS and Na_2SO_3. On adding a great deal of a strong acid to the solution of a thiosulphate, we obtain free sulphur and sulphurous acid. In other words, the free thiosulphurous acid dissociates entirely into these constituents. The difference in the behavior of the salt and the acid is due to the fact that the salt solution contains the thiosulphate mainly in the form of the free ion, $S_2O_3^{--}$, which contains less free energy than the un-ionized form. The free acid, $H_2S_2O_3$, however, is present mainly in the un-ionized form, and this is much less stable—more reactive—contains more free energy.

Thiosulphates are moderately strong reducing agents. When oxidized by weak oxidizing agents, such as iodine in neutral or moderately acidified solutions, they react as follows:

$$2S_2O_3^{--} = 2S_4O_6^{--} + 2\ominus$$

That is, they form tetrathionates (*e.g.*, $Na_2S_4O_6$). The potential of this change is evidently not dependent on the concentration of H^+ or OH^- in the solution. Very strong oxidizing agents, such as chlorine in neutral or acidified solutions oxidize both

the sulphite sulphur and the "free" sulphur to the sulphate stage, according to the equations

$$S_2O_3^{--} + 5H_2O = 2SO_4^{--} + 8\ominus + 10H^+$$
$$4Cl_2^\circ + 8\ominus = 8Cl^-$$

Inserting the inactive sodium ions, and adding these two equations, we obtain

$$Na_2S_2O_3 + 5H_2O + 4Cl_2 = Na_2SO_4 + H_2SO_4 + 8HCl$$

The above reaction shows that the change of thiosulphate to sulphate involves H^+ ion, and hence the (reducing) potential of this change is least in acid solutions and greatest in alkaline solutions. Hence only very strong oxidizing agents will oxidize thiosulphate to sulphate in acid solutions; but in alkaline solutions even a weak oxidizing agent such as iodine (more especially hypoiodite) is able to produce this change, according to the equations

$$S_2O_3^{--} + 10OH^- = 2SO_4^{--} + 5H_2O + 8\ominus$$
$$4I_2^\circ + 8\ominus = 8I^-$$

Inserting $2Na^+$, and adding, we obtain

$$Na_2S_2O_3 + 10NaOH + 4I_2 = 2Na_2SO_4 + 5H_2O + 8NaI$$

A comparison of these equations with the preceding set above will reveal that they are identical except for the fact that in the acid solutions H_2O must be used to secure O^{--} while in the alkaline solution OH^- is used.

Thus it is plain that only weak oxidizing agents, such as iodine, acting upon thiosulphate in neutral or acid solutions, will change the latter to tetrathionate; this observation is of great importance in iodometric titrations.

Concerning the reducing actions of hydrogen sulphide, it is merely necessary to say that the tendency of the change of the sulphide ion (S^{--}) to free sulphur (S°) varies with the concentration of the former. Accordingly, it appears several times (at Nos. 8, 11, and 14) in our table of Oxidation Changes. Hence, sulphides will react with an oxidizing agent in the right-hand column and below lines, 8, 11, or 14. Furthermore, the sulphur may not only be changed to free sulphur, but to higher oxidation stages in accordance with the strength of the oxidizing agent.

Sulphur reacts in alkaline solutions to form sulphides and sulphites essentially, that is a part of the sulphur is reduced from S° to S^{--}, while another part is oxidized from S° to S^{4+}. The general relations involved in such reactions have been discussed in Part I under the heading "Substances which Act Simultaneously as Oxidizers and as Reducers." This behavior of sulphur is not important and hence will not be considered further. The sulphide and the sulphite react further with each other, and they also take up free sulphur—to form a mixture of "yellow" sulphides and thionates, etc.

Chromium.—This element occurs in the following oxidation stages:

Chromium metal, Cr°	Chromic acid (chromates and bichromates) $Cr^{6+}, 3O^{--}$
Chromous ion, Cr^{++}	
Chromic ion, Cr^{+++}	

Only the last two stages, and the changes from one to the other need to be discussed here because the other substances are not commonly used. The oxidation of the trivalent to the hexavalent form takes place in alkaline mixtures according to the equation:

$$(2Cr^{+++}, 3O^{--}) + 4Na^+ + 10OH^- = 2(2Na^+, Cr^{6+}, 4O^{--}) + 5H_2O + 6\ominus$$

It is evident that this change involves OH^- ion: an increase in OH^- ion helps this change. The potential of this change is undoubtedly well above 1.6 volts (as potentials are calculated in our Table). The oxidation is brought about either in fused NaOH (or Na_2CO_3), or in an aqueous alkaline solution (*e.g.*, of NaOH), and by means of mild oxidizing agents even. Thus even iodine (hypoiodite) with a potential of 1.41 volts will act. However for fused mixtures KNO_3 and $KClO_3$ and for aqueous alkaline solutions Na_2O_2 are the most convenient oxidizing agents because they leave no troublesome by-product. The reaction between Na_2O_2 and Cr_2O_3 takes place according to the equations

$$Na_2O_2 + 2H_2O + 2\ominus = 2Na^+ + 4OH^-$$
$$Cr_2O_3 + 4Na^+ + 10OH^- = 2Na_2CrO_4 + 5H_2O + 6\ominus$$

Multiplying the first by 3, adding, and simplifying the resulting equation, we obtain

$$3Na_2O_2 + H_2O + Cr_2O_3 = 2Na_2CrO_4 + 2NaOH$$

Strong oxidizing agents such as $KMnO_4$ and PbO_2 oxidize trivalent chromium to the chromic acid stage even in acid solutions, although the potential of this change in acid solutions is 0.70 volt or less (see table). Chromic salts can also be oxidized electrolytically (at the anode) in acid solutions, the equation for the change being

$$2Cr^{+++} + 7H_2O = H_2Cr_2O_7 + 12H^+ + 6\ominus$$

On account of this potential of the change between trivalent and hexavalent chromium in acid solutions, chromates in acid solutions act as strong oxidizing agents toward most common reducing agents, *i.e.*, all in the left-hand column of our Table above line 30. Note that this does not include chlorides. The equation for the change is the same as that above for alkaline solutions except that H^+ and H_2O are employed in place of H_2O and OH^- respectively (change from alkaline to acid solution!), and that, furthermore, the bichromic acid $H_2Cr_2O_7$ is present instead of the chromic acid H_2CrO_4 (the latter *dehydrates* to form $H_2Cr_2O_7$). With these modifications, the equation appears thus:

$$(2Na^+, 2Cr^{6+}, 7O^{--}) + 14H^+ + 7SO_4^{--} + 6\ominus =$$
$$7H_2O + 2Cr_2(SO_4)_3 + Na_2SO_4 + 3SO_4^{--}$$

We will give the equations for the action of this oxidizer with several reducers.

(*a*) KI: its reaction is

$$2KI = I_2^\circ + 2K^+ + 2\ominus$$

Hence we must multiply the latter by 3 to make the number of electrons formed equal to the number used up in the above equation of the oxidizer. Adding the two equations, we obtain

$$6KI + Na_2Cr_2O_7 + 7H_2SO_4 = Cr_2(SO_4)_3 + 3K_2SO_4 + Na_2SO_4 + 7H_2O + 3I_2^\circ$$

(*b*) $FeSO_4$: its reaction is

$$Fe^{++}, SO_4^{--} = Fe^{+++} + SO^{4--} + 1\ominus$$

To obtain $6\ominus$, we must multiply this equation by 6. Adding the result to the above equation of the oxidizer, we obtain

$$6FeSO_4 + Na_2Cr_2O_7 + 7H_2SO_3 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + Na_2SO_4 + 7H_2O$$

Other equations may be readily arrived at in the same manner.

Halogens.—In considering the ordinary oxidizing or reducing changes of the halogens, we can exclude any consideration of fluorine because the only valence change it undergoes is from 0 to 1^- and since free fluorine is not capable of existence in aqueous solutions (because it reacts thus: $2F_2 + 2H_2O = 2H_2F_2 + O_2$), it is not employed in ordinary operations.

The other halogens—chlorine, bromine, and iodine—in general exist in the following oxidation stages.

THE COMMON HALOGEN COMPOUNDS IN DESCENDING ORDER OF OXIDATION STAGES
(X stands for Cl, Br, or I)

Order	Common form of each oxidation stage	Theoretical elemental ion	Reduction electrons per X
1	HXO_4 Perhalate (*e.g.*, perchlorate, $KClO_4$).	H^+, X^{7+}, $4O^{--}$	0
2	HXO_3 Halate (*e.g.*, chlorate, $KClO_3$)	H^+, X^{5+}, $3O^{--}$	2
3	HXO_2 Halite (*e.g.*, chlorite, $KClO_2$)	H^+, X^{3+} $2O^{--}$	4
4	HXO, Hypohalite (*e.g.*, hypochlorite, KCl O)	H^+, X^+, O^{--}	6
5	Free halogen (*e.g.*, Cl)	X^0	7
6	HX, Halide (*e.g.*, chloride, KCl)	H^+, X^-	8

A few exceptions should be mentioned: Chlorine exists in all the stages shown in the table above, and furthermore in the form of the oxide, ClO_2, chlorine dioxide, in which chlorine is evidently tetravalent. Bromine does not exist in the halite stage, nor in the perhalate stage (and no oxides of bromine appear to be capable of separate existence). Iodine exists in all stages in the table above except the halite stage.

The most important, and the most puzzling, behaviors of the different halogen compounds are those of the free halogens and of the hypohalites—both respectively in acid and in alkaline solution. Hence we will consider these first.

When a halogen is dissolved in pure water, a small amount reacts with water—hydrolyzes—in accordance with the following equation, using Cl for illustration:

$$Cl_2^\circ + H_2O \rightarrow\leftarrow H^+ + Cl^- + HOCl$$

This is a reversible reaction and since the reaction involves H^+ ion, the equilibrium necessarily is dependent, among other factors, upon the H^+ ion concentration. That is, the reaction stops when the H^+ ion concentration has reached a value which together with the corresponding concentrations of the other substances stops the reaction.

Hence, when a base is added to this solution and thus the H^+ ion concentration decreased, more of the free halogen will be able to react to form chloride ion—and HOCl (or a salt of the latter), and accordingly we find that, in alkaline solutions, free halogen changes almost completely to chloride and hypochlorite according to the equation

$$Cl_2^\circ + 2NaOH = NaCl + NaOCl + H_2O$$

We note that 1Cl has changed from Cl° to Cl^-, *i.e.*, has been reduced—while the other Cl has changed from Cl° to Cl^+, *i.e.*, has been oxidized. This phenomenon of the same element acting both as oxidizing and as reducing agent has been discussed in Part I under the heading "Substances which Act Simultaneously as Oxidizers

and as Reducers," and it has been shown there that in acid solutions the potential of the change

$$2Cl^- \rightarrow\leftarrow Cl_2^\circ + 2\ominus .$$

is greater *numerically* than the potential of the change

$$Cl_2^\circ + 2H_2O \rightarrow\leftarrow 2HOCl + 2H^+ + 2\ominus$$

The following table presents the corresponding values for all the halogens. The numerical values are on the basis of the hydrogen pole potential being 2 volts and the values *decreasing* as the reactions written to express oxidation—from left to right—tend to take place with less force (as in the table of "Oxidation Changes.")

Nature of change	Potential in acid solutions ($N/1H^+$)		
	Cl	Br	I
Halide $\rightarrow\leftarrow$ free halogen $2X^- \rightarrow\leftarrow X_2^\circ + 2\ominus$	0.65	0 92	1.37
Free halogen $\rightarrow\leftarrow$ hypohalite . . . $X_2^\circ + 2H_2O \rightarrow\leftarrow 2HOX + 2H^+ + 2\ominus$	0 37	0 41	0 63

It is evident from these values that the material on the left of the upper equation will change *to the right* while the material on the right side of the lower line will change *to the left.* In other words, *in acid solutions, halides react with hypohalites*[1] *to produce free halogen.* The sum of these changes is expressed by the equation (with chlorine):

$$NaCl + NaOCl + H_2SO_4 = Na_2SO_4 + Cl_2 + H_2O$$

But in alkaline solutions, the numerical values of the potentials of these changes have the reverse relations—as is shown in the following table:

Nature of change	Potential in alkaline solution ($N/1OH^-$)		
	Cl	Br	I
Free halogen $\rightarrow\leftarrow$ hypohalite $X_2^\circ + 4(OH) \rightarrow\leftarrow 2(XO)^- + 2H_2O + 2\ominus$	1 57	1 61	1.46
Halide $\rightarrow\leftarrow$ free halogen $2X^- \rightarrow\leftarrow X_2^\circ + 2\ominus$	0 65	0 92	1.37

With this arrangement according to the potentials, the material on the left of the upper equation will react with that on the right of the lower equation, or, *in alkaline solutions, free halogen will react with free halogen to form hypohalite*[1] *and halide.*

[1] Hypohalous acids are all extremely weak (practically not ionized!) and hence changed to salts only in strongly alkaline solutions. The gradation in strength is from I to Cl, hence HOI is neutralized but slightly in alkaline solutions. The *salts* are naturally extensively ionized.

The difference between the potentials, in acid and alkaline solutions, of the change of free halogen to hypohalite is due to the fact that this reaction involves H^+ or OH^- ion and these are obtained from, or *added to* these different solutions with different ease or difficulty. For further discussion of this topic, see Part I: "*Potentials of Changes Involving Hydrogen and Oxygen Ions.*"

The equations for the reaction of free halogens in alkaline solution is the sum of the equations in the preceding table—the first reading from left to right, and the second from right to left. Adding them accordingly, and inserting the inactive Na^+ ion, we obtain (with chlorine)

$$2Cl_2^\circ + NaOH = 2NaOCl + 2NaCl + 2H_2O$$

This striking difference in the behavior of the free halogens in acid and alkaline solutions shows itself again in the behavior of the hypohalites themselves. These substances also can change so as to be reduced (to free halogen or to halide ion) or so as to be oxidized to the halate stage (the intermediate halite stage does not appear to be formed by direct oxidation of hypohalite!). In other words, they will act simultaneously as oxidizer and as reducer provided the potential relations are such as to impel such a change. On account of the fact that the potentials of all the changes possible would have to be considered, a presentation of the potentials will be omitted, and a general statement of their relations only will be made.

In alkaline solutions, we have the following relations:

(*a*) For each halogen, the potential of the change of its hypohalite salt (*i.e.*, free XO^- ion!) to halate is numerically the greatest of all the different possible oxidation changes from hypohalite to halate stage.

(*b*) For each halogen the potential of the change of its free hypohalous acid to halide is numerically the least of all the different possible reduction changes of the hypohalite stage.

(*c*) The potentials for the change from hypohalite to halate are numerically greater than those for the change from hypohalite to halide. Hence these two changes have the proper potential relation for taking place together;[1] and since the greatest potential for their combined action is obtained when the free (un-ionized!) hypohalous *acid* is reduced to halide while the hypohalite *salt* (or ion!) is oxidized to halate, it follows that these are the changes that actually take place when these substances are present, and that the equations for these reactions are

$$HOX + H^+ + 2\ominus = X^- + H_2O$$
$$NaOX + 4OH^- = NaXO_3 + 2H_2O + 4\ominus$$

Multiplying the first by 2, adding, and simplifying, we obtain

$$2HOX + NaOX + 2NaOH = 2NaX + NaXO_3 + 2H_2O$$

The proper conditions for the reaction—*i.e.*, the simultaneous presence of free hypohalous acid and hypohalite salt—are obtained with chlorine by using a solution of sodium bicarbonate or a "suspension" of lime or of magnesia, and bubbling chlorine gas into this. To hasten the reaction the solution is kept warm.

The above-mentioned solutions are very nearly neutral to begin with, and as the reaction uses up OH^- ion, they will maintain their state of near-neutrality—the bicarbonate by evolving CO_2—the others by dissolving more oxide. Since the whole change begins with the free halogen, and ends with halide and halate respectively, we may write the reactions for it without considering the intermediate hypohalite stage. Thus the equations are

$$Cl_2^\circ + 2\ominus = 2Cl^-$$
$$Cl_2^\circ + 12(OH)^- = 2(ClO_3)^- + 6H_2O + 10\ominus$$

[1] See Part I: Notes on Table of Oxidation-changes.

Multiplying the first by 5, adding, and inserting the inactive cations (Na^+), we obtain

$$6Cl_2^\circ + 12NaOH = 2NaClO_3 + 10NaCl + 6H_2O$$

Since, in acid solutions, all halates are stronger oxidizing agents than in alkaline solutions, the above resulting mixture of a halide and a halate will, when acidified, react to form the free halogen again according to the following equations:

$$2\ Cl^- = Cl_2^\circ + 2\ominus$$
$$KClO_3 + 6H^+ + 6\ominus = KCl + 3H_2O$$

Multiplying the first by 3, and adding the result to the last, we obtain

$$6HCl + KClO_3 = 3Cl_2 + KCl + 3H_2O$$

For bromides and iodides the corresponding equations will express the same changes. This reaction between iodate and iodide in acid solutions is made use of in iodimetry because it will stop as soon as the solution has become neutral. Thus it is used to determine the normality of an acid.

Chloric acid (or a chlorate plus an acid) is used frequently as an oxidizing agent, and according to its position in our table (No. 33), it will oxidize all common substances capable of oxidation. It is a much stronger oxidizing agent than nitric acid. In analytical work it is used to oxidize As_2S_3 to arsenic acid—a change which takes place according to the following equations (using method (2) for writing these equations—see Part I)

$$As_2S_3 + 8H_2O = 2H_3AsO_4 + 10H^+ + 10\ominus + 3S$$
$$KClO_3 + 6H^+ + 6\ominus = KCl + 3H_2O$$

Multiplying the last equation by 5 and the first by 3, and adding the results, we obtain on simplifying

$$3As_2S_3 + 9H_2O + 5KClO_3 = 6H_3AsO_4 + 9S + 5KCl$$

Perchlorates are formed by anodic oxidation (electrolysis) of chlorates in neutral or acid solutions—according to the equation

$$ClO_3^- + H_2O = ClO_4^- + 2H^+ + 2\ominus$$

They are also obtained by heating chlorates moderately: a portion will react thus,

$$4KClO_3 = 3KClO_4 + KCl$$

while another portion—the relative amount of which increases with the temperature—reacts to evolve oxygen gas.

Perchlorates and perchloric acid are very stable and do not act as oxidizing agents except to extremely strong reducing agents. Hence, they are not employed as oxidizing agents in solutions, but merely as dry salts in explosives.

Periodates are formed by the action of moderately strong oxidizing agents (*e.g.*, chlorine) on iodates in alkaline solutions; also by heating dry iodates, and by anodic oxidation of iodates. Periodates and periodic acid are not so stable as perchlorates or perchloric acid, and they act as weak oxidizing agents. Thus zinc reduces periodic acid to free iodine, but mercury scarce reacts with it. This phenomenon of higher oxidation stages having lesser oxidizing powers than lower stages has been discussed in Part I.

In conclusion, attention should be called to the fact that for the changes from halide to free halogen

$$2X^- = X_2^\circ + 2\ominus$$

the potentials are the same in acid and alkaline solutions, because they do not involve H^+ or OH^- ion. But the potentials of all oxidation-reduction changes of oxy-halogen compounds change with the H^+ or OH^- concentration of the solutions in which they occur, and they have values which place them in our Table with reference to their corresponding "halide-halogen" line, as follows: *above* in alkaline solutions; *below* in acid solutions.

Furthermore, corresponding changes of all compounds of chlorine, bromine, and iodine, *except perhalates*, would occupy, in our Table, the same order from top to bottom as the "halide" halogen-potentials—that is, ranging downward in the order—iodine, bromine, chlorine. For instance, iodic acid is a weaker oxidizing agent than chloric—just as iodine is a weaker oxidizing agent than chlorine.

Manganese.—This element exists in the following oxidation stages:

Manganous compounds	MnO, $MnSO_4$ — Mn^{++}
Manganic compounds	Mn_2O_3, $MnCl_3$ — Mn^{+++}
Manganites	MnO_2, $CaMnO_3$ — Mn^{4+}
Manganates	MnO_2, K_2MnO_4 — Mn^{6+}
Permanganates	Mn_2O_7, $KMnO_4$ — Mn^{7+}

The salts of the first and last stage are stable in acid solutions, and unstable in alkaline solutions, while the reverse is true of the other oxidation stages.

Freshly precipitated manganous hydroxide is flesh-colored, but turns dark from the formation of $Mn(OH)_3$ by the oxygen of the air. With strong oxidizing agents, it will naturally change to a higher oxidation stage. Thus with permanganate in neutral solutions, it will change to MnO_2 according to the equations (using method (2), Part I for writing these equations)

$$Mn^{++} + 2H_2O = MnO_2 + 4H^+ + 2\ominus$$
$$KMnO_4 + 4H^+ + 3\ominus = MnO_2 + 2H_2O + K^+$$

Multiplying the first by 3, the second by 2, adding the results, inserting the inactive anions (*e.g.*, SO_4^{--}) and simplifying, we obtain

$$3MnSO_4 + 2H_2O + 2KMnO_4 = 5MnO_2 + K_2SO_4 + 2H_2SO_4$$

In order to prevent the solution from becoming acid, we add solid zinc oxide to it: this serves also to convert the MnO_2 to $ZnMnO_3$—zinc manganite—the hydrated MnO_2 functioning as an acid of the formula H_2MnO_3. The above reaction is used for the quantitative determination of Mn^{++} ion.

Manganates are formed by fusing together a compound of one of the lower oxidation stages of Mn together with sodium carbonate, and an oxidizing agent. The latter can be either *air*, or KNO_3, etc. With air and MnO_2, the reaction takes place in accordance with the equation (dualistic formulas to express the relations—see beginning of Part I)

$$MnO_2 + O + Na_2O{\cdot}CO_2 = Na_2O{\cdot}MnO_3 + CO_2$$

The green manganate will dissolve, and remain intact, in alkaline solutions; but in acid solutions it changes by the oxidation of some of its molecules and the simultaneous reduction of others—according to the equations

$$(2Na^+, Mn^{6+}, 4O^{--}) + 4H^+ + 2\ominus = Mn^{4+}O_2^{--} + 2H_2O + 2Na^+$$
$$MnO_4^{--} = MnO_4^- + 1\ominus$$

Multiplying the last by 2, adding the inactive anions (bicarbonate, HCO_3^-), we obtain

$$3Na_2MnO_4 + 4H_2CO_3 = MnO_2 + 2NaMnO_4 + 4NaHCO_3$$

It is advisable to use CO_2 to acidify the mixture because the excess is easily disposed of. Otherwise, any acid will do for this purpose.

In a solution acidified so as to be normal in H^+ ion, a solution of permanganate containing 1 gram-molecule per liter has the potential given in No. 32 of our table. It is evidently one of the most powerful oxidizing agents at our disposal, and it will oxidize everything in the left column of the table above line 32.

Line 32 presents the potential of the change

$$Mn^{++} + 4H_2O = MnO_4^- + 8H^+ + 5\ominus$$

or

$$MnSO_4 + 4H_2O + K^+ = KMnO_4 + SO_4^{\ -} + 8H^+ + 5\ominus$$

The reaction is quantitative and exact, and hence forms the basis of a great many titrometric processes. A few examples will be given.

(*a*) Oxidation of Oxalic Acid—the equation for its oxidation is (see under "Carbon" above)

$$(COOH)_2 = 2CO_2 + 2H^+ + 2\ominus$$

The equation for the reduction of permanganate in acid solution is

$$KMnO_4 + 8H^+ + SO_4^{--} + 5\ominus = MnSO_4 + 4H_2O + K^+$$

Multiplying the first by 5, the last by 2, adding the results, inserting $1SO_4^{--}$ to both sides, and dropping $10H^+$ from both sides, we obtain

$$5(COOH)_2 + 3H_2SO_4 + 2KMnO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

(*b*) Oxidation of Nitrites—see under "Nitrites."

(*c*) Oxidation of ferrous salts—see under "Iron."

(*d*) Oxidation of hydrogen peroxide—see under "Oxygen."

In alkaline solutions, permanganates exert a much feebler oxidizing tendency—so that the change

$$MnO_4^- + 1\ominus \rightarrow\leftarrow MnO_4^{--}$$

on the basis employed in our Table, has a potential of 1.39 volts, or a position between the iodide iodine and the ferrous-ferric potentials (Nos. 22 and 23 in the Table). If the alkaline or neutral solution contains any manganous salt, the permanganate will react with the latter to form MnO_2 (see above).

Iron.—The only oxidation-reduction change of iron which is of importance is the change

$$Fe^{++} \rightarrow\leftarrow Fe^{+++} + 1\ominus$$

the potential of which is in our Table (No. 23). From this it is seen that all the substances above 23 in the left column will reduce ferric salts, while those below 23 in the right column will oxidize it. Simple oxidation reduction equations with iron salts have been given in Part 1.

It will suffice here to give the equations for the oxidation of ferrous salts by HNO_3 and by $KMnO_4$.

(*a*) With HNO_3, the equations are

$$Fe^{++} \rightarrow Fe^{+++} + 1\ominus$$

$$HNO_3 + 3H^+ + 3\ominus = NO + 2H_2O$$

Multiplying the first by 3, adding, and inserting the inactive anions ($3SO_4^{--}$ and $3\ NO_3^-$) we obtain

$$3FeSO_4 + 4HNO_3 = 3Fe\begin{cases} NO_3 \\ SO_4 \end{cases} + NO + 2H_2O$$

or $$6FeSO_4 + 8HNO_3 = 2Fe_2(SO_4)_3 + 2Fe(NO_3)_3 + 2NO + 4H_2O.$$

(*b*) With $KMnO_4$, the equations are

$$KMnO_4 + 8H^+ + 5\ominus = K^+ + Mn^{++} + 4H_2O$$
$$Fe^{++} = Fe^{+++} + 1\ominus$$

Multiplying the first by 2 and the last by 10, adding the result and inserting the inactive anion (SO_4^{--}), we obtain

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5Fe_2(SO_4)_3$$

The valence of iron in its double cyanides—*e.g.*, potassium ferrocyanide, $K_4Fe(CN)_6$, and potassium ferricyanide, $K_3Fe(CN)_6$—is sometimes puzzling and hence may be considered here.

The simplest way to recognize the valences of the iron in these compounds is to consider them to be split into their "constituent" simple cyanides—thus $K_4Fe(CN)_6 = 4KCN + Fe(CN)_2$. It is evident that we have a bivalent iron cyanide in this case. Similarly,

$$K_3Fe(CN)_6 = 3KCN + Fe(CN)_3$$

and this shows that we have a trivalent iron cyanide in the last case. Hence the names—*ferrocyanide* for the former and *ferricyanide* for the latter.

The cyanides can be easily changed from one to the other. By anodic oxidation, ferrocyanides can be changed to ferricyanide according to the equation

$$Fe(CN)_6^{----} = Fe(CN)_6^{---} + 1\ominus$$

The potential of this change—on the scale in our *Table*—is 1.60 volts (between Nos. 21 and 22 in the table).

The oxidation of ferrocyanide can also be effected by means of chlorine—according to the equations

$$Cl_2^\circ + 2\ominus = 2Cl^-$$
$$Fe(CN)_6^{----} = Fe(CN)_6^{---} + 1\ominus$$

Multiplying the second by 2, adding and inserting the inactive cations (*e.g.*, K^+), we obtain

$$Cl_2 + 2K_4Fe(CN)_6 = K_3Fe(CN)_6 + 2KCl$$

The reduction of the ferricyanide is also easily accomplished—either by cathodic reduction, or by the action of mild reducing agents such as iodides, sulphides, etc.—the equation for the reduction by iodides being

$$2I^- = I_2^\circ + 2\ominus$$
$$Fe(CN)_6^{---} + 1\ominus = Fe(CN)_6^{----}$$

These two can be combined just like the preceding

SECTION XXI

ELECTROLYSIS

By Donald M. Liddell[1]

When a direct current passes through a chemical compound, either in solution or fused, if the voltage exceeds a certain minimum, decomposition will take place, and the composing elements will be set free at the two poles, or new combinations will be formed with or at the electrodes.

It is possible also that slight chemical changes take place when electric currents are passed through certain solids, but these changes, if they occur, at least are not of such magnitude as to be of commercial value.

Liquids divide themselves into three classes: those which conduct currents without decomposition (as liquid metals), those which do not conduct the current; those which decompose under the influence of the current (electrolytes). Water probably comes in the second class, non-conductors, but absolutely pure water is so difficult of preparation that the point is obscure Distilled water is, at least, almost a non-conductor.

Electrical Units.—Neglecting the c.g.s. definitions, the practical electrical units may be defined as follows: The ampere is such a current that passed through a silver nitrate solution in water, it will deposit 0 00111827 g. of silver per second. One ampere passing for 1 sec. is defined as a coulomb. The ohm is the unit of resistance. It is the resistance offered by a column of mercury at 0°C., 14.4521 g. in mass, of a constant cross-section and 106.3 cm. in length (also defined as the resistance of a column 106.29 cm. long, 1 sq cm. in cross-section at 0°C.). The volt is the unit of pressure and 1 volt will produce a steady current of 1 amp. through 1 ohm resistance. The watt is the unit of energy; 1 amp. flowing for 1 sec. under a pressure of 1 volt requires the expenditure of 1 watt of energy.

Electrochemical Equivalents.—The amount of any given substance that is set free, providing a certain minimum voltage is exceeded, is a function only of the time and the amperes of current that are passed through the electrolyte, and this quantity is not altered by the combination in which the given substance exists, providing the valence is not altered. Thus, 0.01976 g. of copper are deposited if 1 amp. passes through a cupric salt for 1 min., whether it be cupric sulphate, cupric nitrate, or cupric chloride. In the same way, 0.06709 g. of silver will be deposited by 1 amp. flowing for 1 min. and 60×0.06709 or 4.0258 g. by 1 amp. flowing for 1 hr. These electrochemical equivalents are proportional to the atomic weights divided by the valence. A short table of these equivalents is given.

[1] Weld & Liddell, Engineers and Economists, New York, N. Y.

Element	Atomic weight O = 16	Valence	Chemical equivalent	Electro-chemical equivalent, grams per second	Grams per ampere-hour
Electropositive					
Aluminum	27.00	3	9 00	0 00009327	0.3358
Antimony	120.20	3	40 07	0 00041525	1.4949
Bismuth	209.00	3	69 67	0 00072202	2 5992
Cobalt	58.97	2	29 48	0 00030558	1 1000
Copper (ic)	63 57	2	31 78	0 00032942	1 1858
Copper (ous)	63 57	1	63 57	0 00065885	2.3718
Gold	197.20	3	65.73	0 00068122	2 4524
Hydrogen	1 008	1	1 008	0.00001045	0 03764
Iron (ic)	55 84	3	18.61	0 00019296	0 6946
Iron (ous)	55 84	2	27.92	0 00028934	1.0416
Lead	207.20	2	103.6	0 00107371	3.8654
Mercury (ic)	200.60	2	100 30	0.00103944	7.4840
Mercury (ous)	200.60	1	200 60	0.00207888	14 9680
Nickel	58 68	2	29 34	0 00030079	1 0946
Potassium	39.10	1	39.10	0 00040512	1 4584
Silver	107.88	1	107.88	0.00111827	4 0258
Sodium	23.00	1	23 00	0 00023838	0.8582
Tin (ous)	118.70	2	59.35	0 00061510	2.2144
Zinc	65.37	2	32.68	0.00033869	1.2192
Electronegative					
Bromine	79.92	1	79 92	0 00082824	2.9814
Chlorine	35 46	1	35.46	0 00036749	1.3230
Iodine	126 92	1	126.92	0 00131539	4.7353
Nitrogen	14 008	3	4.67	0 00004840	0.1742
Oxygen	16 00	2	8 00	0 00008291	0 2985

1 amp. per square decimeter = 9 29 amp. per square foot = 0.0645 amp. per square inch.

1 amp. per square foot = 0.006944 amp. per square inch = 0.1076 amp. per square decimeter.

1 amp. per square inch = 144 amp. per square foot = 15 50 amp per square decimeter.

In case an equivalent is not given it can easily be found by proportion. Thus, magnesium has an atomic weight of 24.32 and a valence of 2. Its chemical equivalent is therefore $24.32 \div 2 = 12.16$. The amount of magnesium deposited per ampere-hour is therefore Ag : Mg :: 107.88 : 12.16 :: 4.0257 : x.

The general theory of electrolysis is pointed out by one of the calculations noted above, that the atomic weight must be divided by the valence. It is believed that all electrolytes dissociate in solution into parts called ions, which carry electric charges proportioned to the valence. All bivalent ions carry identical charges; all trivalent ions carry identical charges, which are one-and-a-half as great as those carried by a bivalent ion. These ions may be simple or

complex. In copper sulphate they are Cu^{++} and SO_4^{--}, in silver sulphate, Ag^+, Ag^+, SO_4^{--}, and in ammonium sulphate, NH^{4+}, NH^{4+}, SO_4^{--}, both positive and negative ions in this last case being complex.

This dissociation into ions takes place without the aid of the electric current but is only complete if the solution be very dilute. When electrodes are immersed in an electrolyte the positively charged ions are attracted to the negatively charged electrode and there lose their charge, similarly the negatively charged ions are attracted to the positive electrode. At the electrodes the ion is either deposited, or sets up secondary reactions. In the electrolysis of copper sulphate, the copper is deposited as a plating on the positive electrode (cathode) while the SO_4 ion, if the negative electrode (anode) be soluble, dissolves it, as $Cu^{++} + SO_4^{--} = CuSO_4$. If the anode be insoluble (platinum, graphite), the sulphate ion reacts with the water of the solution $H_2O + SO_4^{--} = H_2SO_4 + O^{--}$.

According to this theory there is no real conduction through an electrolyte, as there is through a metallic conductor, but the charged ions arriving at the electrodes partially neutralize and thus diminish their charges and permit a further flow of electricity from the generator to the electrode.

Energy Required for Electrolysis.—As is well known, the formation of chemical compounds from the elements usually is accompanied by the evolution of heat, the so-called heat of formation. Some of the heats of formation are shown in an accompanying table. These are "molecular heats," *i.e.*, those evolved by reactions involving gram quantities equal to the atomic weights (or multiples thereof), the final mass in grams of the compound produced by the reaction giving out these quantities of heat being equal to the compound's molecula weight.

The small figures under the heats of combination show roughly the combining quantities in grams. They are the atomic weights rounded off, and are probably at least as accurate as the values given for the heats of formation.

Referring again to the table, in general it will be found that these heats divided by the valence of the base stand roughly in the same order in each column, and it will also be found that the basicity of the substances decreases from top to bottom of the table. It is also true that in each list made by dividing combining heats by valences and arranging the metals in order of the figures thus obtained, a metal will displace in chemical compounds any metal following it, but will not affect any that precedes it. Thus iron or lead will throw out copper from solution but copper will not throw down either lead or iron. In general, such a series is spoken of as an electrochemical series and the elements in it are said to be electronegative to those that follow and electropositive to those that precede. The usual order given is: + K, Na, Mg, Mn, Zn, Cd, Fe, Co, Ni, Pb, Sn, Bi, Cu, Hg, Ag, Pt, Au, H, Sb−. But it can be seen from the various columns of the accompanying table that the order is dependent somewhat upon the acid radical and with metals very close the order is not an invariable; thus, cadmium may be electropositive to cobalt in one electrolyte and electronegative to it in another. It is also dependent to some extent upon concentration.

Since, as has already been stated, the amount of metal deposited per hour is a function of the amperes only, and since it requires the same energy to break down a compound that it gives out when formed, it is obvious that if the heat of formation be known, the minimum voltage at which the compound will break down with insoluble electrodes can be calculated.[1]

[1] This voltage is equal to the counter e m f of a battery whose electrodes are whatever the anode and cathode would be if the designated reaction went on and where the activating solution is the

MOLECULAR HEATS EVOLVED IN FORMING

Element	Oxides	Chlorides	Nitrates	Sulphates
Potassium, K' . .	98,200	105,700	119,000	344,300
	(78 + 16)	(39 + 35 4)	(39 + 14 + 48)	(78 + 32 + 64)
Sodium, Na'	100,900	97,900	110,700	328,100
	(46 + 16)	(23 + 35 4)	(23 + 14 + 48)	(46 + 32 + 64)
Barium, Ba'' .	133,400	197,100		
	(137 + 16)	(137 + 71)		
Calcium, Ca'' .	131,500	169,900	202,000	317,400
	(40 + 16)	(40 + 71)	(40 + 28 + 96)	(40 + 32 + 64)
Strontium, Sr''	131,200	184,700		330,200
	(87 + 16)	(87 + 71)		(87 + 32 + 64)
Manganese, Mn''	90,900	112,000		249,400
	(55 + 16)	(55 + 71)		(55 + 32 + 96)
Zinc, Zn'' . . .	84,800	97,400	131,700	229,600
	(65 + 16)	(65 + 71)	(65 + 28 + 96)	(65 + 32 + 96)
Cadmium, Cd''	66,300	93,700		219,900
	(112 + 16)	(112 + 71)		(112 + 32 + 96)
Iron, Fe'' . .	65,700	82,200		234,900
	(56 + 16)	(56 + 35 4)		(56 + 32 + 96)
Cobalt, Co'' . . .	64,100	76,700		228,900
	(59 + 16)	(59 + 76)		(59 + 32 + 96)
Nickel, Ni'' . .	61,500	74,700		228,700
	(58 5 + 16)	(58 5 + 71)		(58 5 + 32 + 96)
Lead, Pb'' . . .	50,800	83,900	105,400	215,700
	(207 + 16)	(207 + 71)	(207 + 28 + 96)	(207 + 32 + 96)
Tin, Sn''	70,700	80,900		
	(118 + 16)	(118 + 71)		
Copper, Cu''	37,700	51,400	81,300	181,700
	(63 6 + 16)	(63 6 + 71)	(63.5 + 28 + 96)	(63 5 + 32 + 96)
Mercury, Hg''.	21,500	53,300		165,100
	(200 + 16)	(200 + 71)		(200 + 32 + 96)
Silver, Ag' .	7,000	29,000	28,700	167,100
	(216 + 16)	(108 + 35 4)	(108 + 14 + 48)	(216 + 32 + 96)
Gold, Au'''	−11,500	22,800		
	(394 + 48)	(197 + 106 5)		
Hydrogen, H' . .	69,000	22,000	48,800	192,200
	(2 + 16)	(1 + 35 4)	(2 + 14 + 48)	(2 + 32 + 96)

It requires 96,494 coulombs to deposit 1 g. = equivalent of any metal. (This quantity is usually known as a Faraday and denoted by F.)

Then if n be the valence of the compound, the energy to break up the compound $= nEF$ watts and Q calories per second Since 1 cal. = 4.20 watts

$$nEF = Q \times 4.2. \quad \text{Since } F = 96{,}494$$

electrolyte under consideration. What is meant by "whatever the anode and cathode would be" is this. In the simple electrolytic analysis of copper (a copper nitrate solution with platinum anode and cathode) the instant deposition starts the counter e.m.f. is not platinum against platinum in a solution of unequal concentration, but copper (cathode) against platinum (anode).

$$E = \frac{4.2Q}{96.494n} = \frac{Q}{22.975n} \quad \text{(Thompson's rule).}$$

This is not quite true, a more accurate statement being given by the Gibbs-Helmholz equation

$$nEF = Q \times 4.2 + T\frac{dE}{dT}$$

in which T = absolute temperature and $\frac{dE}{dT}$ is the temperature coefficient of the electromotive force. This coefficient is usually small and Thompson's rule suffices for practical purposes.

Conversely it follows that if the minimum decomposition voltage of a compound using insoluble anodes is known, the heat of formation can be calculated. It also follows that the theoretical deposit of metal per killowatt-hour may be calculated in advance, though 100 per cent efficiency is never reached in practical work It is, however, a most valuable guide, for since many of the heats of combination are published, it is possible to get an approximate idea of the power that is going to be required per ton of material produced.

It is also possible to calculate exactly how much of any product should be given by the number of amperes at one's disposal, and to check up in this way both the genral power efficiency and the ampere efficiency of a plant.

With soluble anodes the case is entirely changed. If copper is being dissolved from an anode as fast as it is being precipitated on the cathode, the energy of solution is equal to the energy required for decomposition, so that the current expended is only that needed in overcoming the resistance of the circuit and the internal resistance on the electrolytic cell.[1] It can be seen why it is preferable to carry on electrolytic processes using soluble anodes to carrying on the same process by dissolving the metal by purely chemical means and then depositing it using insoluble anodes.

If the potential difference between two insoluble electrodes is less than the decomposition voltage of the electrolyte, a "diffusion" current will still flow. This is a small current carried by actual migration of ions and tends to produce differences in concentration of the solution until such time that the tendency to produce further changes is exactly balanced by the tendency to diffuse. The migration velocities of various ions has been measured. Some of them are as follows:

Ion Migration Velocities, Centimeters per Second
(Potential gradient 1 volt per centimeter, 18°C.)

H	0.00326	OH	0.00180
NH_4	0.00066	I	0.00069
K	0.00067	Cl	0.00068
Ag	0.00056	NO_3	0.00064
Na	0.00045	ClO_3	0.00057
Li	0.00035	$C_2H_3O_2$	0.00042

Non-ionized colloidal particles may apparently also carry charges (see p. 288) by actual physical migration.

Osmotic and Solution Pressures.—There is, however, an absolute measure for an electrochemical series, independent of the acid radical. When any substance dissolves in any solvent where there is not infinite miscibility, after a

[1] Including in this "internal resistance of the cell" the effect of osmotic and electrolytic solution pressures, to be spoken of later.

time there is a certain back pressure against further solution, known as osmotic pressure. In most respects this is strictly an analogous phenomenon to vapor pressure, the osmotic pressures (in dilute solutions) being proportional to the number of molecules dissolved, both in the case of a single un-ionized salt in varying quantities, or in the case of two un-ionized salts of different molecular weights. Moreover, as in gases, total pressure is the sum of partial pressures.

The reason for specifying "un-ionized substances" is that with metallic salts in aqueous solution the pressures are always greater than should be expected from the number of molecules involved. The accepted explanation, the only one we can see that fits all the known facts, is that in extremely dilute solution all of the salt dissociates into its metallic and non-metallic radicals, and that these parts, so far as osmotic pressure goes, exercise the same effect as the molecules. This is only true in very dilute solution, and evidently only a small portion of the molecules present are dissociated in ordinary solutions. These are the ions already mentioned, and while many of them are elementary substances, it must never be lost to sight that their physical properties are not those of the elements, beginning with the most important fact that each ion carries an electric charge.

Electrolytic Solution Pressure.—In a solution after ionization the positive charges (on the metallic ions) and the negative charges (on the acid radicals) are in equal numbers. The condition of the solution is unchanged. But if a plate of iron be immersed in water and a portion of it passes into solution, the ions passing into solution would be positively charged, and an equal amount of negative electricity would appear on the plate. The tendency of a metal to ionize and to pass into solution is known as its electrolytic solution pressure and when elements are ranged in order of their decreasing electrolytic solution pressures we have an absolute electrochemical series, independent of the radicals present.

Some of these pressures are, in atmospheres:

Zinc 9.9×10^{13}	Cobalt 1.9	Copper. . 4.8×10^{-10}
Cadmium $2\ 7 \times 10^{6}$	Nickel .. . 1.3	Mercury.. $1\ 1 \times 10^{-16}$
Iron... 1.2×10^{4}	Lead . $1\ 1 \times 10^{-3}$	Silver . . $2\ 3 \times 10^{-17}$
	Hydrogen .. $9\ 9 \times 10^{-4}$	

This ionizing tendency is opposed by the osmotic pressure; by the difference in electric potential generated; and by the fact that in aqueous solution the ions usually form an insoluble compound by reacting with the water, which coats the metal and stops further action.

$$Zn^{+} + 2H_2O = Zn(OH)_2 + 2H^{+}$$

If the hydroxide is not insoluble, action will go merrily on, as in the well-known reaction,

$$2K + H_2O = 2KOH + H_2$$

Therefore we may postulate that the solvent action of an acid on a metal is mainly not a direct one, but consists in dissolving the insoluble hydroxides formed by most metals.

From these considerations we can see that the requisites for depositing a pure metal from a mixed electrolyte are that we have a current sufficiently high to exceed its solution pressure, and that no metal of lower solution pressure be present and that

we do not have a high enough current to deposit those metals of higher solution pressures. On the other hand, we can deduce at this point that to deposit an alloy from a mixed solution it is only necessary to have a current of great enough potential to overcome the higher solution pressure and of sufficient dilution in the element of lower solution pressure that the amperes used cannot be carried by the number of ions present, together with an anode of the alloy desired, and an electrolyte in which all its components are soluble.

The voltage difference caused by solution pressure and osmotic pressure is

$$E = \frac{RT}{nF} \log_e \frac{P}{C}$$

where R is the gas constant in joules per degree, T the absolute temperature, v the valence, F the Farady, P the solution pressure, and C the osmotic pressure.

In an electrolytic cell the voltage of the cell is

$$E = \frac{RT}{n_1F} \log_e \frac{P_1}{C_1} - \frac{RT}{n_2F} \log_e \frac{P_2}{C_2}$$

where the subscripts indicate the different metals.

And for a uniform metal immersed in a segregated solution, the e m.f. between two points on the metal will be $E = \frac{RT}{nF} \log \frac{C_1}{C_2}$ where C_1 and C_2 are the ionic concentrations at the two points.

Overvoltage.—In those processes where hydrogen is liberated at the cathode it has been found that the potential difference necessary for electrolysis is greater than the theoretical amount for the decomposition of the given electrolyte by varying quantities dependent on the cathode material. That is, the electrolyzing potential for two portions of the same electrolyte will be greatly different if a platinum cathode is used in one case and a lead cathode in the other. Taking a platinum-black cathode as 0.0 (as the voltage is less with this cathode than with any other), other values (according to Caspari) are as follows:

Values of η in volts

Hg	1.3	Sn	1.15	Cu	0.19
Pb	1.3	Ni	1.00	Pt (bright)	0.07
Cd	1.22	Zn	0.80		

No satisfactory explanation is known for this phenomenon.

Passivity and Anode Overvoltage.—If oxygen is evolved at the anode there are also overvoltage phenomena. These are usually inconsiderable, yet where millions of pounds of metal are deposited, as at the New Cornelia Copper Co.'s plant at Ajo, Ariz., or the Chile Copper Co.'s works at Chuquicamata, Chile, the anode overvoltage may be a considerable monetary item, and can by no means be neglected. Some of these anode overvoltages are: Nickel, 0.05; iron, 0.24; platinum black, 0.24; lead peroxide, 0.28; graphite, 0.40; bright platinum, 0.44 volts.

There is sometimes an even more serious anode disturbance, known as passivity. That is, in certain electrolytes certain metals show no tendency to dissolve completely when used as anodes, even though one would expect them to. Those exhibiting this quality in the highest degree are: aluminum, chromium, cobalt, iron, molybdenum, and tungsten.

Various hypotheses have been advanced for this. As summarized in 1916 by the Faraday Society the chief are: (1) The formation of a surface gas film; (2) the formation of an oxide film; (3) conversion of the surface metal into an allotropic modification of which the electrolytic solution pressure is low (4) the velocity of ionization or hydration of the ion is retarded.

Polarization.—Somewhat akin to passivity, if the first hypothesis be correct, is the phenomenon known as polarization, when minute gas bubbles gather on either anode or cathode or both and greatly raise the cell resistance. The phenomenon was of the utmost importance when batteries were a large source of power and many batteries employed depolarizers, for instance, potassium bichromate in the Poggendorff cell, which reacted chemically with the hydrogen formed.

In general polarization disappears when the cell is allowed to stand, partly through slow coalescence of the small gas bubbles into those large enough to escape, partly by solution of the gases in the electrolyte. But there is this important point to remember, that polarization often develops slowly and cell resistances are therefore often lower during the first few hours of running than they are later, and one important commercial installation proved of little value because of increased costs due to polarization resistance. In all experimental electrolytic work, be sure the cells are run long enough for polarization and passivity effects to develop before drawing final conclusions.

Systems of Refining.—All refining operations may be carried on either by "multiple" or "series" arrangements. In the first all anodes (and all cathodes) in any individual tank are in parallel, that is, they all have a direct connection to the busbars. In the series system only the two headplates in each tank are connected to the source of current supply, one being the cathode, the other the anode. Between them are arranged as many parallel plates as one pleases (up to the point where the resistance of a single tank becomes too high). The side of each plate toward the tank anode then becomes a cathode and receives a deposit, while the side of each plate toward the tank cathode becomes an anode and is eaten away, each plate (theoretically) moving toward the anode end of the tank by its own thickness as the refining progresses.

Suspending these intermediate plates has always been a great deal of a problem. There must be a certain amount of tank space below them into which may settle the insoluble impurities of the metal being refined. The Nichols Copper Co. suspends its cast series copper "flap jacks" by hooks; the Baltimore Copper Smelting & Rolling Co. holds its rolled plates by grooved sticks that grip the sides. In each of these systems if the plate moved over the theoretical distance (its thickness) during refining, the original support would be detached from the new plate and it would fall. Consequently a certain proportion of metal even though it be only a strip along the edge must be left unrefined as a support to the newly deposited metal and there is sometimes difficulty in parting the two.

There is always a little current lost by its going underneath the plate and traveling through the slimes in the series tank. The plates must be rolled or cast of very even thickness, or else some will finish before others, and thereafter pure copper will be eaten away and redeposited.

While the horsepower efficiency[1] of the series tank is greater than that of the multiple, the process requires much closer attention to detail and more managerial

[1] The ampere efficiency is lower due to lost current through the slimes and other causes, but the resistance between plates is less, and circuit resistances are smaller, so more copper is deposited per horsepower-hour in series than in multiple refining, *i.e.*, the horsepower efficiency is greater.

ability and only two copper refiners use it. The series process has been tried for lead refining but was discarded, and I am told was tried for electrolytic iron production and found wanting in simplicity.

It is obvious that a single series tank will have a much higher resistance than a single multiple tank, though between individual plates the resistance is less. But whichever is used, these internal resistances cannot be cut down below a certain limit. They are part of the essential cost of the process. But the circuit resistance is a dead overhead. So, apart from using large cross-sections and good mechanical contacts to cut down circuit losses, one will throw many tanks into series to cause the tank resistances to bear a high ratio to the circuit resistance, and also to get an economical type of generator. For this reason, small electrolytic units are often built with several cells in series where it would be mechanically possible to install a single tank.

Tank Arrangement.—In metal-refining (copper, lead, etc.) it is now very common to build tanks in long rows with a common side to each two tanks and on this to place a triangular copper conductor. All of the anode lugs of one tank rest on it and all the cathodes of the next tank. Each small section of the bar (except for the end anode or cathode) will then carry half the current of one electrode. It will be objected to at first sight that the triangular rod will not give a good contact with the electrode, but as a matter of fact it does. Furthermore, the rods should be kept somewhat oily, as most tank-room atmospheres are corrosive. The thin skin of oil will not affect the contact. Figure 1 shows the arrangement of tanks and electrodes referred to.

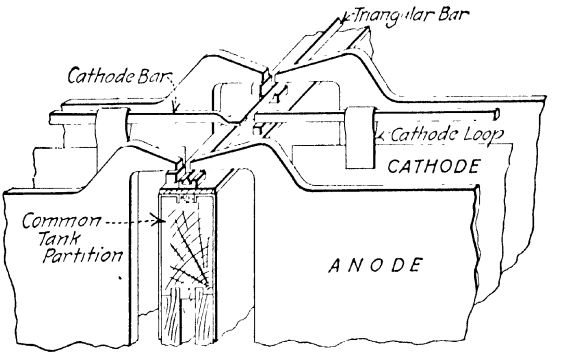


FIG. 1. Tank and electrode arrangement.

As said above, the tank arrangement in an installation will be figured to give an economic ratio of tank to circuit resistance. The amperes to be used is a matter of dividing the ampere-work to be done by the number of tanks. (One ampere will deposit 0.00111827 g. of silver per second in one cell. If put through 20 cells in series deposits 20 times as much.) The outside circuit will be made as short as possible, to cut down line resistance, and will be calculated to that size where the increased interest on the cost of the extra copper becomes less than the cost of the power saved.[1]

[1] The Institution of Electrical Engineers (British) uses a formula for calculating size of conductors which is independent of the price of copper. It is $C = 2\,6.4^{0.82}$ or

$$\log C = 0.82 \log A + 0.415$$

where C = current in amperes, A = area in thousandths of a square inch. While undoubtedly sizes given by this formula are safe, when copper is cheap it pays far to exceed mere safety, and I believe that the price of copper must enter into the calculation where large currents are being carried.

Electrodes.—Both anodes and cathodes for metal refining are shown in an accompanying illustration. Anodes are usually supported by lugs cast on the anode (not, however, in series processes). Cathodes are supported by loops or hooks. The cathode is originally a starting sheet, which may be of the metal to be deposited, in which case the starting sheet is usually melted with the deposit, or it may be of other material, and the deposited cathode metal is later stripped off.

Special cases of this last are those processes in which tubes are made by depositing metal on a rotating cylindrical mandrel, or where a wire is made by stripping from a spirally grooved mandrel. A similar special case where the deposit is not stripped is where a wire is plated as it is drawn through a bath.

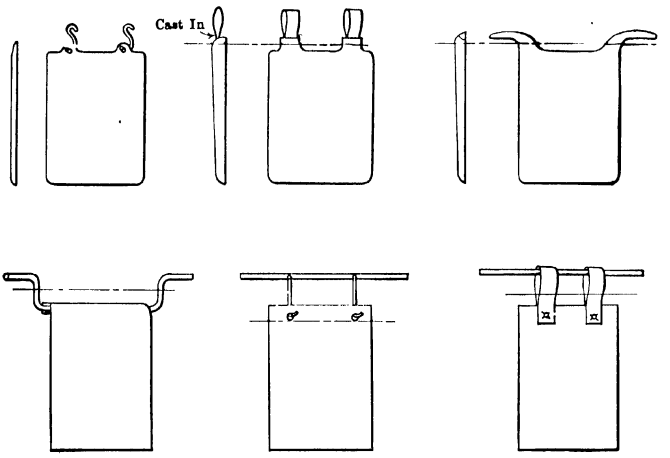


FIG. 2.—Electrode shapes.

The entire bottom of a tank may be made a cathode, as in the Thum silver refining process, or the cathode may be a puddle of mercury, as in some variations of electrolytic sodium-hydrate manufacture.

Anode Materials.—The materials for insoluble anodes must be chosen first with regard to insolubility, second, with regard to their overvoltage, already spoken of. To show that it is no small problem it may be mentioned that the Chile Copper Co. tried over 3,600 different compositions for insoluble anodes. For large scale work the usual choices lie between graphite, hard lead, one of the ferrosilicon alloys (tantiron, duriron, corrosiron, or the like) fused magnetite, platinum gauze or the Fink cuprosilicide anode.

If hard lead is used, casting appears to be preferable to rolling, as the cast skin appears to be somewhat more resistant than the rolled. There are marked differences in graphite anodes, probably due to the binder material used, and because one make has proved unsatisfactory for certain work is no reason for abandoning the trial of graphite anodes. Several makes should be tested. Magnetite anodes, which were given a most extensive trial at Chuquicamata, eventually were discarded as being uncommercial. They broke too easily when being handled, and under the particular conditions existing at Chuquicamata, developed a tendency to crack and split.

When using anodes of low conductivity it is helpful to cast them hollow and fill the interior with copper. This insures a much better distribution of current over the surface of the anode and cuts down the circuit resistance at the same time.

From the electrolytic standpoint it is of advantage to have insoluble anodes in motion. This decreases the polarization because it sweeps away the gas bubbles mechanically, and in addition it keeps a layer of more constant concentration at the anode surface. This again is a mere balancing of commercial factors, the cost of the power to move the anodes and the mechanical complexities necessary being weighed against the electrolytic advantages.

Some ordinary soluble anode shapes are shown in Fig. 2. There is not much to be said about soluble anodes except that uniformity of surface is desirable to prevent excessive corrosion at projecting points, uniformity of thickness of all the anodes is essential that all the anodes in a tank may finish at the same time, uniformity of composition is important that the rate of solution may be the same over the entire anode and the lugs or other supporting members should have an ample factor of safety.

Cathode Materials.—Ordinarily, in metal refining, the cathode will be the same material as the metal deposited. This is not true in zinc refining simply because there is decided tendency to corrosion of the anode at the solution line (where the oxygen of the air helps the electrolyte in dissolving zinc) and if zinc cathodes were used they would often cut through and drop down into the tank causing short-circuits and broken tanks.

Nor are silver cathodes used in the Thum-Balbach silver refining process, as it would tie up too much silver and the lower anode resistance would nowhere nearly offset the interest charge thus created. In the case of zinc electrolysis it would be more convenient to have an all zinc cathode which could be melted entire, rather than to have to strip the zinc, but the labor cost of stripping is less a disadvantage than those evils ensuing from cut cathodes. It is again a balancing of economic factors, which after all, is what differentiates the chemical engineer from the chemist.

In copper refining, the metal is deposited on "starting sheets," which are thin copper sheets which have been deposited on greased copper plates and then stripped off. Ordinarily grooved sticks are run around the edges of the starting sheet blank, preventing deposition there and making the sheets easier to strip from the blank. As a matter of practical interest it should be noted that the current should be on as the blanks are placed in the electrolyte so that deposition may begin at once, otherwise the grease comes off slowly into the electrolyte and when the current is turned on the new deposit becomes firmly adherent and the starting-sheet blank is spoiled.

What is said of copper starting sheets can be considered typical. Lead and tin sheets can be made in similar manner, but it is cheaper to cast them. Zinc sheets may be made, but as already said, it is better not to use them, but to use aluminum instead.

In plating, the article to be plated is the cathode. As this is a quality process, and imperfections are as a rule exaggerated in plating, all mechanical imperfections should be removed before plating, after which all grease must be taken off with soap or some alkali. After the article has been cleaned it should preferably not be handled again with bare hands. If articles to be plated can be kept in motion results are usually superior to those obtained where they are motionless

This is in part due to the keeping the electrolyte stirred so that a solution of uniform composition is presented to the electrodes; in part to the irregular shapes of articles to be plated, which makes the distance of various parts from the anode unequal, which effect is minimized by moving the cathode (of course an article will be

suspended in such manner as itself to minimize this effect); and probably to the fact that mechanical work is performed in this way on the deposited material, thereby improving its texture.

In this matter of plating, two recent interesting novelties are to remove the cathode repeatedly from solution, and then reimmerse it,[1] and to deposit thin films of nickel from time to time in a copper plate, thereby greatly increasing its tensile strength.[2] The results of this latter innovation seem due to retarding the growth of crystals through the presence of the interdeposited metal.

Another kink of various applications is the use of a mercury cathode. Because of the tendency to form amalgams mercury can be used as a cathode to attain some results otherwise impossible. For instance, mercury can be used to take up sodium and by having the cathode stirred constantly and project under a partition into a separate compartment containing water, the water in the second compartment gradually becomes changed to caustic soda, while if sodium chloride solution is the electrolyte used in the other cell, chlorine is given off at the anode.

The use of rotating cathodes has already been referred to. Much higher current densities can be used with rotating than with stationary cathodes, and the deposit is of better quality. In part this improvement can be attributed to keeping the electrolyte about the cathode thoroughly mixed and probably in part as in plating to the mechanical work performed on the deposit, the effect being analogous to cold rolling or drawing. The effect of the mechanical work done by the electrolyte against the cathode is often reinforced by the use of buffing pads against the deposited metal.

Seamless tubes are formed of copper, of iron and of nickel on rotating cathodes. Usually annealing to remove hydrogen is necessary in order to make them less brittle particularly if the tube is to be reduced by drawing.

Cell Resistance.—This is composed chiefly of the resistance of the electrolyte. To reduce this the electrodes will be placed as close together as the mechanics of the process will permit, *i.e.*, in metal refining the danger of bridging the gap either by an accidental excrescence on the anode, or the growth of a "tree" on the cathode due to some local condition. In the electrolytic production of gases the exigencies of the collecting apparatus will dictate the space. Ths electrolyte will also be heated to cut down its resistance to the point where the cost of heating outweighs the saving in power or until adverse chemical reactions enter.

The saving in current by heating the electrolyte may be entirely counterbalanced by undesirable effects along other lines. Thus, in silver and lead refining too high temperatures increase the acid-radical losses beyond tolerance, and if the tanks are an asphalt or sulphur compound, the tanks will not stand up, while with zinc deposition with insoluble anodes the electrolyte must be refrigerated to avoid re-solution losses.

There is also a counter e.m.f., due to the electrolytic cell acting as a battery. This resolves itself into a question of the anode and cathode materials and the concentrations of the electrolyte around them, or the differences of electrolyte if it is a two-fluid cell.

That is, to take a specific case, anode copper, because of its impurities, has not the same electrolytic solution pressure as has the refined cathode copper, while the electrolyte about the anode tends constantly to become different from that about the cathode, and as a result there is a counter e.m.f. set up.

There is also unquestionably an adsorbed gas film on most anodes and also on the cathodes if gas is being evolved there. Even where a metal is being deposited on the

[1] C. P. Marsden, Brit. pat. 142,432 of 1919

[2] *Chem. and Met. Eng.*, p. 961, Nov. 23, 1921.

cathode some hydrogen is usually occluded, which renders it necessary to anneal many electrolytic deposits that are to be used without remelting. Such are the seamless steel tubes already referred to. I have been told by one experimenter who annealed electrically *in vacuo* that he obtained hydrogen equivalent at normal pressure and temperature to seven times the volume of the electrolytic nickel from which it was derived. The so-called protective colloids also form a layer about the cathode that sends up the tank resistance enormously(see p. 744).

Acid Radical.—In the selection of a salt for any refining process the following considerations will weigh. The acid radical must be fairly cheap and stable. The salt must be soluble. If impurities are to be taken out as slime they should be insoluble in the acid used. The tank lining should not be affected by it. Poisonous fumes should not be given off, and the cathode should not readily redissolve.

Plating stands on a little different ground in that it is a quality process. Therefore, the cost of the salt used is not vital and in small operations poisonous fumes may be controlled.

This, however, brings up one important matter. It should always be considered in commercial operation whether any impurity may exist in the electrolyte that may give rise to poisonous fumes either by anodic oxidation or cathodic reduction, and if there is such a possibility, the operation must be conducted where good ventilation exists and without any close attendance. A typical case is the generation of arsine in electrolyzing spent copper electrolytes, this reaction taking place at the cathode when the copper is almost all deposited

Diaphragms.—Where it is desirable to retard diffusion, for instance in a cell where iron is being deposited on a cathode from a ferrous chloride solution which was being oxidized to ferric chloride at the anode, or where an organic addition agent is being used at the cathode a porous diaphragm is placed in the cell. The classic material for this purpose is porous earthenware.

Diaphragms are also made of "filtros," apparently a silicon hydrate product, which permits rapid ionic diffusion, but does not allow rapid intermixture of the anolyte and catolyte. Diaphragms can also be made of asbestos board for temporary experimental use, but if they are to be in use long they require strengthening with a wooden grid or other support. If metal supports are used the experimenter may find he is working with two or three series cells (see p. 738) instead of a single diaphragm cell, the side of the metal support toward the anode becoming a series cathode, etc.

Tank Materials.—The usual tank materials are hard or soft lead (extensively used in multiple copper refining); wood heavily asphalted (lead, zinc and both series and multiple copper refining); slate (series copper refining); glass (gold refining and electrochemical industries); porcelain (silver refining and electrochemical industries); portland cement acidproofed with some bituminous material or plain for neutral and faintly alkaline solutions; or a sand-sulphur mixture.

If hard-lead is used 10 per cent of antimony appears to give the best results. Whether hard or soft lead is used, lead of the same composition as the tank lining should be used for burning the joints

Asphalt-lined tanks are subject to the disadvantage that high temperatures cause the tank lining to run. To reduce the viscosity of the lining finely powdered silica may be added to the asphalt. Slate, glass and porcelain all have the disadvantage

of being breakable. Slate tanks have the additional one of having to be built up, so that there are joints that must be carefully sealed, usually with some bituminous composition. Portland-cement tanks can be made to stand either acids or alkalies, as explained on page 842, but not the two alternately.

Of the sulphur-sand mixes, the one introduced by Charles S. Bradley may be considered typical. His mix is composed of 1 part sulphur and 1.4 parts sand ground to pass at least a 60-mesh screen. The mixture is then heated to about 150°C., where it flows well and is far enough above the melting point of sulphur (114°C.) to avoid sudden chilling. But the mixture must not be heated as high as 156°C. for at that temperature sulphur begins to thicken, and at 180°C. becomes so viscid that it will no longer flow.

Commercial Electrolytes.—Copper is refined commercially from a sulphate electrolyte containing about 3 per cent copper and 12 per cent of free acid. Theoretically the power would be cut in half by using cuprous chloride rather than copper (ic) sulphate, but other considerations render the sulphate the cheaper. The same electrolyte is usually used for copper plating (1½ lb. copper sulphate crystals and ½ lb. of sulphuric acid per gallon of water) but copper cyanide is also used. Silver is both plated and refined with a nitrate electrolyte (5 per cent Ag, 0.1 per cent free HNO_3 and some copper). Potassium-silver cyanide is also used for plating. Gold is refined using gold chloride electrolyte containing a high percentage of hydrochloric acid (Wohlwill process) about 25 to 30 oz. gold and the same amount of free hydrochloric acid per cubic foot. There is an interesting feature in this process that an alternating current is passed simultaneously with the direct current used for deposition, the object of the alternating current being to shake off the silver chloride formed on the anodes. Potassium-auric cyanide is usually used for gold plating baths.

Lead refining is done with lead fluosilicate solutions acidulated with hydrofluosilicic acid and containing some addition agent such as glue or gelatin (Betts process). The electrolyte contains about 8.50 per cent Pb and 11.5 per cent of total H_2SiF_6, both free and combined, and about 0.18 per cent of free HF. Siemens & Halske have patented the use of lead perchlorate in free perchloric acid as an electrolyte, using peptone as the most desirable addition agent. The process is said to be in use at the Hagener accumulator works,[1] but as a true refining bath from impure anodes it appears inferior to the fluosilicate. Nickel is refined using nickel-sulphate solutions slightly acidulated with boric acid, but nickel-ammonium sulphate (5 to 8 per cent solution) is usually used for plating. Cobalt, so far as my knowledge goes, is not refined electrolytically. Kalmus recommends the following plating solution: Cobalt sulphate ($CoSO_4$) 312 g.; sodium chloride, 19.6 g.; water, 1 liter; boric acid almost to saturation. Use current up to 100 amp. per square foot. Iron is commercially electrodeposited from a ferric-chloride solution. Theoretically ferrous-sulphate or ferrous-ammonium sulphate would be preferable, but so far as my own experiments go, it is impossible to keep the deposited iron low enough in sulphur to make the process commercial. The only use of iron known to me as an electroplate is its deposition on engraved copper plates as a hard protective coat that can easily be removed, when it begins to wear. Ferrous sulphate, ferrous-ammonium sulphate, iron alum, and double cyanides may all be used for this work.

Platinum is electroplated from platinic-chloride and ammonium-platinic chloride (acidulated with citric acid and carrying an excess of ammonium chloride) solutions. But it is not satisfactory, as the anodes do not dissolve readily, and the bath is soon

[1] Rideal, "Electrometallurgy," D. Van Nostrand, p. 88.

too depleted to work well. Palladium is plated on mirrors and other scientific apparatus from palladic-chloride solutions, using a moving carbon anode.

Zinc is deposited on a large scale from zinc-sulphate solutions using insoluble anodes and usually aluminum cathodes (Anaconda, Mont., Park City, Utah). During the World War it was also electrolytically refined using anodes of Prime Western spelter. The process is not commercial ordinarily as there is not a sufficient margin of price between Prime Western and High Grade, and there is no precious-metal content to bear the refining toll as there is (ordinarily) in impure copper. "Electrogalvanizing" may be done with zinc-chloride, zinc sulphate or double-cyanide solutions.

As a rule zinc solutions must be carefully freed from cadmium, copper, nickel and cobalt by agitation with atomized zinc. At Anaconda the electrolyte contains about 5 per cent zinc and 2½ per cent free sulphuric acid, and the current density is about 23 amp. per square foot.[1] At Trail, B. C., the electrolyte carries about 7.5 per cent of zinc and 2 per cent of acid on entering the tanks and discharges at 3 to 5 per cent of zinc and 5 to 7 per cent of free acid. Current density is about 24 amp. per square foot and tank temperature about 30 to 45°C.[2] At Anaconda about 1 to 1½ oz. of glue per ton of zinc produced is added to the electrolyte. This is typical of the small amount of these addition agents necessary to give a dense cathode with small crystals.

Copper is recovered on a large scale, *i.e.*, millions of pounds per year, by leaching with sulphuric acid and precipitating the metal by electrolysis with insoluble anodes. At the Chile Copper Co.'s installation at Chuquicamata, the ore is brochantite, an oxysulphate of copper, so that there is a constant surplus of acid produced by the leaching operation, which permits discarding a portion of the electrolyte from time to time in order to prevent undue contamination (see p. 746). The electrolyte normally carries: Cu, 50.44 g. per liter; SO_3, 122.75; free H_2SO_4, 28.0; Fe, 3.71; Mn, 0.07; P, 0.06; As, Sb, 0.0; CaO, 0.8; MgO, 3.32; Al_2O_3, 1.61; Na_2O, 21.6; K_2O, 5.0; Cl, 11.52 g. per liter. It is freed from chlorine before electrolysis by agitating with cement copper in revolving drums, which forms cuprous chloride that is then filtered out and the copper precipitated on scrap iron thus reforming cement copper.

The work at Ajo has been described in great detail by Tobelmann, Potter and Gross.[3] The process consists essentially in leaching with sulphuric acid (and such ferric sulphate as is present); reduction of the solution with sulphur-dioxide gas or cement copper and electrolysis. The cement copper referred to is produced by passing the discarded electrolyte over scrap iron. Acid is purchased from the C. & A. smelting plant.

The copper leaching and electro-deposition processes of Höpfner and of Siemens & Halske, usually described at great length, are now only interesting chemical curiosities. The former is a cupric-chloride leaching process, the latter a ferric-sulphate leaching process, but it is time some of the metallurgical dead were decently interred, and ancient history may be consulted for further details.

Cadmium is recovered from zinc-solutions and electrolytes by chemical means. It may be plated from an ammonium-cadmium sulphate solution, although the process has no commercial application to my knowledge. Antimony is refined using antimony tri-fluoride solution with antimony anodes.

A curious phenomenon in connection with antimony-deposition is that if amorphous antimony is deposited from a solution of 1 part of antimony ter-chloride in 5 or 6 parts of hydrochloric acid, of specific gravity 1.12, the amorphous mass changes to crystalline antimony under the influence of sudden heating, or of a sudden blow

[1] F. Laist, *Trans.* A. I. M. E., February, 1921 meeting.
[2] E. H. Hamilton, *Trans.* Am. Electrochem. Soc., Vol. **32**, p. 317, 1918.
[3] *Trans.* A. I. M. E., Vol. **55**, p. 830; Vol **60**, p. 20.

with the evolution of sufficient heat to scorch paper or wood, and of a cloud of vapor, apparently from occluded electrolyte.

Bismuth is difficultly refined, as its great tendency to form complex salts in solution usually results in evolution of hydrogen, and spongy deposits. While Foerster and Schwabe claim to have obtained good deposits from a fluosilicate solution it is believed that the only commerical installations now operating in the United States are using bismuth chloride containing enough free hydrochloric acid to prevent precipitation as oxichloride.

Tin is being refined electrolytically at Perth Amboy using a tin-chloride-sulphate solution with an organic addition agent but the greatest use of electrolytic processes for tin is in its recovery from tin scrap. The tin scrap is used as the anode and polished steel plates as the cathodes. The electrolyte is a strong solution of sodium hydroxide (about 8 per cent) which is regenerated, as it carbonates, by calcium hydroxide. The solution is kept hot, preferably over 150°F., and current is passed until the last of the tin is removed from the iron The process has not proved adapted to tin cans from garbage as it has not proved possible to clean them economically and the electrolyte soon becomes unworkable while the slime containing the tin is foul and often will not melt, though much time and money have been spent on efforts to treat "swill cans." It is believed that detinning with dry chlorine offers some advantage in cost over electrolytic detinning for all applications. For electrolytic tin plating a bath containing 2½ to 3 per cent of stannous chloride, 5½ to 6½ per cent of ammonium oxalate and 0.35 per cent of free acetic acid is probably as good as any, but it is difficult to get bright dense adherent deposits. Iron and steel should be given a copper strike before plating with tin.

Deposition of Alloys.—Usually when a current is passed through a mixed solution, only the least electropositive metal is precipitated. This may be due to not reaching the higher decomposition voltage, or it may be that the more electropositive metal is deposited and then redissolves in the solution, precipitating some of the less electropositive metal as it dissolves. That this separation can be made, is of course the basis for all electrolytic refining processes.

Nevertheless it is sometimes desirable to be able to deposit alloys. The conditions for doing so are: (1) If the current be so strong that the more electropositive metal has not the time to dissolve before a further deposit over it of both metals occurs; (2) if the solution used has a nearly identical decomposition voltage for both metals. (3) If the proportion of the more electronegative metal be so small that it is exhausted by electrolysis as fast as it can be replaced by diffusion, so that the more electropositive metal, as deposited, has nothing to act upon.[1]

Purification of Electrolyte.—Possibly the greatest problem of the electrolytic refiner is the contamination of his electrolyte. Purification may be effected in various ways, some examples of which have been given. Thus, the electrolyte used for electrolytic detinning is regenerated chemically by calcium hydroxide. Copper solutions (in refining) can be partially regenerated by plating out all the copper with insoluble anodes, crystallizing out the nickel and sending the acid back to the tank house. Nevertheless, there comes a time in commercial operations when all that can be done is to recover if possible what valuable metals are in a portion of the electrolyte either by chemical or electrochemical means, and send the treated portion to the sewer.

[1] For plating formulas, moulding compositions, stripping baths, etc., see Watt's "Electrometallurgy," D. Van Nostrand, or McMillan and Cooper's "Electrometallurgy," C. Griffin & Co.

This problem of electrolyte contamination is not alone a concern of the hydro-electrometallurgist. The thermo-electrical worker likewise has his troubles. Though chemically purified alumina is put into the aluminum bath, the impurities build up until part of it must be thrown away. Magnesium chloride baths finally become unusable because of oxide produced by secondary reactions.

In general it may be said that what is the greatest concern of the commercial operator is usually the smallest worry to the amateur experimenter, and much work has been done and published that is of no great immediate value because the electrolytes were not run continuously for a long enough period for all the troubles due to impure baths to develop and the problems of electrolyte regeneration are unsolved, and indeed unknown.

Electrolysis with Fused Electrolytes.—While the conductivity of fused electrolytes is usually higher than that of aqueous solutions, the horsepower efficiency is much lower. This is largely due to the following causes: (1) Volatilization of the deposited metal; (2) chemical side-reactions involving reactions usually impossible in aqueous solution—for instance the formation of the sub-chloride, CaCl, in the electrolysis of calcium chloride; (3) cloud formation, or the dissipation of the precipitated metal through the fused electrolyte as a cloud. The use of the lowest feasible temperatures minimizes this. (4) The re-solution of the metal in the electrolyte.

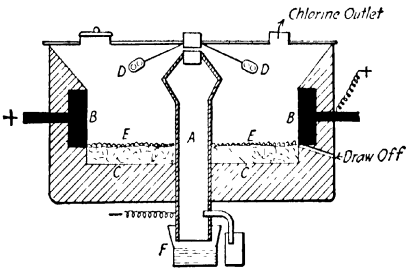


FIG. 3.—Cell for producing sodium.[1]

Aluminum is produced by the use of a bath consisting of cryolite (sodium-aluminum fluoride) in which alumina is dissolved as needed, about 20 per cent should ordinarily be kept in the mixture. Because of the expense of replacing the bath when contaminated, purified alumina is used. The bath is contained by a carbon or alumina lining, preferably the latter and run at 750 to 850°C. The potential drop is usually 5 to 7 volts, and it requires about 10 hp.-hr. per pound of aluminum.

Magnesium is usually recovered by electrolysis of the fused anhydrous chloride. If a pure magnesium-chloride electrolyte is used the metal will float to the top of the bath and burn there to oxide, unless it is trapped by inverted steps on the cathode, or some similar form of construction. A mixture of magnesium and potassium chlorides (with preferably a little ammonium chloride avoids this). The natural potassium-magnesium chloride (carnallite) is therefore in favor where obtainable for magnesium production. Too high a voltage deposits potassium at the same time, while even small amounts (0.05 per cent) of iron in the electrolyte cut down the cell efficiency tremendously through alternate reduction and oxidation.

Sodium and potassium may both be recovered from the electrolysis of the molten hydroxides. In both the metal is lighter than the electrolyte and is caught by having

[1] Courtesy D. Van Nostrand Co., from Rideal's "Electrochemistry and Electrometallurgy."

a tube suspended over the cathode and closed with a movable cover in which the metals collect. Sodium has a high surface tension and an interesting use is made of this fact. The metal is ladled out in iron ladles with small holes through which the metal cannot pass (because of its surface tension). Any retained electrolyte, however, flows away freely through the holes. In sodium recovery electrolysis is said to be conducted at about 320°C. using a current of about 170 amp. per square decimeter.

A commercial cell for the recovery of sodium from direct electrolysis of sodium chloride is shown in the illustration. (This shows one of the devices for trapping a metal lighter than the electrolyte.) A circular furnace is employed, lined with firebrick, containing an annular graphite and a hollow iron cathode, surrounded at its upper extremity by a watercooled hood.

On electrolysis the liberated sodium flows up through the watercooled hood and down through the hollow space into a collecting vessel.

Sodium chloride is also electrolyzed using a molten lead cathode, the cathode subsequently being treated with steam for the production of caustic soda.

Calcium is prepared from fused calcium chloride or from a mixture of calcium chloride and calcium fluoride (the latter used because it lowers the melting point of the mix). Since the melting point of the metal is higher than that of the electrolyte it is possible by close control of the temperature of the electrolyte to produce calcium as a solid, depositing it on a so-called "contact electrode." This is an electrode (usually iron and usually a circular plate) which can be raised as the metal is deposited, thereby keeping the separation distance between the electrodes constant. The metal is quenched in petroleum and the porous mass thus obtained is remelted to free it from chloride. It is said that about 10,000 amp. per square decimeter are used with a resulting e.m.f. of 20 to 30 volts. Strontium and barium can also be produced by electrolysis of the fused chlorides.

Electrodes.—In Heroult furnaces 30 amp. per square inch may be allowed for carbon electrodes, 50 amp. for other types of furnace, and 150 amp. per square inch for graphite electrodes.

Electrothermal Processes.—Iron and zinc smelting, the preparation of various ferro alloys, the manufacture of graphite, the reduction of phosphorus and silicon, and the formation of carbon-disulphide, carborundum, the oxysilicides of carbon and many carbides and borides is carried on in the electric furnace, but these seem to be merely thermal processes requiring extremely high temperatures, and not electrolytic processes, and so are not treated here. "The Electric Furnace" by J. N. Pring, Longmans, Green & Co., gives a good review of these processes.

A thermal use of the electric current, but one which must be mentioned, is the trick of using an alternating current as well as a direct in work with fused electrolytes. The electrolysis is performed by the direct current, while the alternating exerts a heating effect only.

SECTION XXII

CATALYSIS

By Hugh S. Taylor[1]

Introduction.—Temperature, pressure, solubility and the electric current are the normal agencies whereby the chemical engineer seeks to promote the chemical activity of the substances with which he is concerned. In constantly increasing measure,[2] modern industrial chemistry is making use of the catalytic agent as an auxiliary for the more ready promotion of chemical reaction. Thus, nitrogen and hydrogen manifest but little reactivity toward one another under varying conditions of temperature or pressure when brought into contact with one another without a catalytic agent. In the presence of reduced iron, or, better in the presence of reduced iron intimately admixed with one or more reduced metals as, for example, molybdenum, nitrogen and hydrogen, over a wide range of temperature, react to form ammonia, pressure increasing the equilibrium concentration of ammonia obtainable. Pressure, temperature or solubility are insufficient to bring about the saturation of an unsaturated liquid fat by means of hydrogen gas. In the presence of finely divided reduced nickel, however, ready saturation of the most diverse oils occurs at temperatures below 250°C. with the production of hard fats suitable for edible purposes or for the manufacture of hard soaps. The operation of the electric current, in, for example, the preparation of per-salts such as persulphates or perborates is modified by the addition of a small quantity of a fluoride, a greatly enchanced yield resulting. Other electrolytic preparations may be similarly catalyzed.[3]

The characteristics of the catalytic agent may be briefly summarized and illustrated as follows:

1. A catalytic agent accelerates (or retards) the velocity of a chemical reaction, itself remaining unchanged in chemical composition when the cycle of operations is completed. Normally, the concern of the chemical engineer is with catalysts which speed up the reaction process, with the so-called *positive catalysts*. Occasionally, as in the addition of such substances as sodium pyrophosphate, hydrofluosilicic acid and various organic compounds to hydrogen peroxide solutions, to diminish the velocity of decomposition of the peroxide, *negative catalysts* or retarding agents are utilized. The participation of the catalyst as an intermediate compound in the cycle of operations is not excluded, but a true catalytic agent must be regenerated in its original chemical form on completion of the reaction of cycle. Thus, sulphuric acid is a catalyst in the dehydration of alcohol to yield ether, although, as shown by Williamson, an intermediate stage in the

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[2] For the history of catalysis consult Rideal and Taylor: "Catalysis in Theory and Practice," Chap. 1., Macmillan, London, 1919

[3] See Rideal and Taylor, *loc. cit.*, Chap. XII.

process may be realized in which ethyl-sulphuric acid may be isolated. The final production of ether is accompanied by the simultaneous regeneration of sulphuric acid.

$$C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O. \quad (1)$$
$$C_2H_5HSO_4 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4 \quad (2)$$

The catalytic substance may change its physical state in the course of the process. Thus, a smooth stranded platinum gauze employed as an accelerator of the oxidation of ammonia by atmospheric oxygen to oxides of nitrogen changes its physical condition; the strands becoming pitted with minute craters in which, under the microscope, deposits of finely divided platinum may be observed.[1]

2. It follows as a corollary of the previous characteristic that small quantities of the catalytic agent are adequate for the promotion of reaction between large quantities of the interacting substances. A square foot of platinum gauze is sufficient for the oxidation of sufficient ammonia to supply oxides of nitrogen to a lead-chamber process sulphuric-acid plant having a capacity of 500 tons of acid per day. The intervention of side reactions frequently results however, in a diminished activity of the catalyst material requiring therefore, its renewal (see, also, p. 754, under "Catalyst Poisons").

3. The catalyst, normally, promotes the establishment of the same equilibrium position that is attained by the manifestation of the chemical forces in absence of the catalyst; the position of equilibrium is governed by the same factors of temperature and pressure as hold in absence of the catalyst. Thus, in the interaction of steam and carbon monoxide

$$CO + H_2O = H_2 + CO_2$$

the reaction is reversible and the reaction constant

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]}$$

at varying temperatures in presence or absence of a catalyst is the same and has the values

$T°C$ =	400	500	600	700	800	1200
K =	0 05	0 1	0 3	0 6	0 9	2 13

High temperatures favor the formation of carbon monoxide as manifested in the water-gas generator; low temperatures favor the production of hydrogen and carbon dioxide; but in the latter case the reaction velocity is slow. In presence of catalytic agents such as oxide of iron, the velocity is accelerated enormously. Use is made of this in the manufacture of hydrogen from water gas. Let us assume that 200 vols. of steam and 100 vols. of water gas (50 vols. H_2 + 50 vols. CO) react at 500°C. In accordance with the equilibrium equation

$$0\,1 = \frac{(200 - x)(50 - x)}{(50 + x)(x)}$$

where x is the number of volumes of carbon monoxide or steam which have reacted to produce hydrogen and carbon dioxide, the gases issuing from the catalyst at equilibrium will be composed approximately of H_2O = 153 vols.; CO = 3 vols.; CO_2 = 47 vols.; and H_2 = 97 vols. a composition identical with that which would have been obtained had the gases proceeded slowly to equilibrium in absence of the catalyst.

Similarly with regard to the influence of pressure upon the equilibrium position. The following table gives the concentration of ammonia in true equilibrium with nitrogen and hydrogen ($N_2 + 3H_2$) at different temperatures under pressures of 1, 100 and 200 atmospheres in presence or absence of a catalyst.

[1] See RIDEAL and TAYLOR, p. 96. PARSONS, *Jour. Ind. Eng. Chem.*, 1919, Vol. 2, p. 550.

Pressure in atmospheres	Equilibrium amounts of NH_3			
	550°C.	650°C.	750°C.	850°C.
1	0 077	0 032	0 016	0 009
100	6 70	3 020	1 540	0 874
200	11 90	5 710	2 990	1 680

Apparent exceptions to the unchangeability of the equilibrium position by the presence of the catalyst medium have frequently been observed. Thus, in the case just cited, Jellinek[1] from a study of the role of iron as catalyst, concluded that if the gases were removed rapidly from the catalyst, concentrations of ammonia in considerable excess of those demanded by the equilibrium could be obtained. It was shown, however, that iron can absorb or dissolve considerable quantities of ammonia, which would be given up on modification of the reaction conditions, for example, by sudden release of the pressure. It is obvious, therefore, that under such circumstances the concentration of ammonia in the solid catalyst phase will be quite definite and may be distinct from that in the surrounding gas phase. Under such circumstances, the laws of equilibrium in a two phase system will apply.

In catalytic reactions in homogeneous systems, also, apparent exceptions are known. Thus, in the interaction of an acid and an alcohol to yield an ester it was shown by Berthelot and Paen de St. Giles, that the reaction constant, in absence of catalysing acid was

$$K = \frac{(H_2O)(CH_3COOC_2H_5)}{(C_2H_5OH)(CH_3COOH)} = 4$$

Lapworth and Jones[2] showed that this value was by no means constant in presence of varying quantities of hydrogen chloride acting as a catalyst. With increasing strength of acid the value rose steadily to nearly 9 in a system in which the ratio H_2O (total water): HCl was 4.65. In such cases the apparent variation in K is explainable on the assumption that the active masses of the reacting species do not correspond to the total concentrations present, or, alternatively, it may be assumed that the participation of the reaction constituents in secondary reactions modifies the active masses taking part in the reaction studied.

For true equilibrium, in a single reaction system, it is demanded by the laws of thermodynamics that the equilibrium position remain unchanged. For, otherwise, it would be possible to bring about *perpetuum mobile* by working alternately with and without the contact substance; the conversion might thus be carried backwards and forwards indefinitely and so, work might be accomplished in a way without fall of temperature, in contradiction to the laws of thermodynamics."[3]

4. Granted that the equilibrium constant, K, remains unchanged in presence or absence of catalyst, it follows, since K is composite of k_1 and k_2, the reaction constants of the forward and reverse reactions,

$$K = k_1/k_2$$

[1] *Zeit. anorg. Chem.* 1911, Vol. **71,** p. 121.
[2] *Jour. Chem. Soc.*, 1911, Vol. **99,** p. 1427.
[3] Van't Hoff, "Lectures on Theoretical Chemistry," 1898, p. 215.

that the catalyst must influence the velocity of the two opposed reactions in an equilibrium process to the same degree. This observation is of importance in industrial operations. Thus, a catalyst which accelerates the combination of sulphuric dioxide and oxygen will also accelerate the decomposition of sulphuric trioxide if brought into contact with the catalyst at a concentration in excess of the equilibrium concentration of the substance at the given temperature of operation. Similarly, acids which accelerate esterification processes similarly catalyse the reverse process of hydrolysis.

5. It is maintained by some that a catalyst cannot initiate a reaction, but may only modify the velocity with which a reaction already occurring may take place. By others, this view is warmly contested and the opinion is held that the catalyst may play a profound part in bringing substances to reaction. From the technical standpoint the question is relatively unimportant, and owing to the wide range of catalytic action it would be difficult to devise experimental tests in which all possibilities of catalytic agency were excluded.

Types of Catalytic Action and of Catalysts.—In the following table an attempt has been made to classify the various types of catalytic reaction, to summarize the various types of catalysts which are active in each class and to illustrate their application in operations of technical importance.

Reaction process	Type of catalyst	Exemplification in Industrial Practice
Oxidation	Metals, especially the platinum metals	(*a*) Contact sulphuric-acid process using finely divided platinum on a suitable support (*b*) The oxidation of ammonia using a platinum gauze. (*c*) The preparation of formaldehyde, using copper or silver (see dehydrogenation).
	Oxides	(*a*) Lead chamber process, employing a gaseous catalyst, oxides of nitrogen. (*b*) Contact sulphuric acid manufacture with iron oxide catalyst. (*c*) Chance-Claus process of sulphur recovery. Oxide of iron as catalyst. (*d*) Purification of illuminating gas Hydrated oxide of iron as catalyst. (*e*) Surface combustion processes Refractory oxides as catalysts.
	Salts	(*a*) Deacon chlorine process. Copper chloride as catalyst. (*b*) Oxidation processes in the dye industry. Mercury and copper salts as catalysts (*c*) Drying of oils. Metallic soaps as accelerators.
Hydrogenation	Metals	(*a*) Hydrogenation of Oils. Nickel and platinum as contact agents. (*b*) Fine organic chemical industry *e.g.*, synthesis of cyclohexane, reduction of organic compounds, nickel as catalyst.
	Oxides	(*a*) Hydrogenation of oils. Nickel oxide as catalyst (especially at elevated pressures; see Ipatiev).
Dehydrogenation	Metals	(*a*) Cracking of oils. Nickel, copper, iron, aluminum as catalysts. (*b*) Dehydrogenation of alcohols. Copper, silver and nickel as catalysts.
	Oxides	(*a*) Cracking of oils, Al_2O_3 and TiO_2 as catalyst. (*b*) Dehydrogenation of alcohols, ZnO, SnO, CdO and MgO as catalysts.
Nitrogen fixation	Metals and metal-oxide mixtures	(*a*) Ammonia synthesis. Reduced iron, iron-molybdenum, iron-potash, nickel-sodium as contact agents. (*b*) Cyanide formation. Reduced iron as catalyst (*c*) Arc process of oxide of nitrogen formation. Metal electrodes as negative catalysts (*d*) Nitride formation (Serpek process). Iron, copper, chromium, molybdenum, as catalysts.

Reaction process	Type of catalyst	Exemplification in Industrial Practice
Hydration and hydrolysis.....	Acids	(*a*) Hydrolysis of glycerides, soap and candle industry. Sulphuric, sulphonic (Twitchell reagent) acids as catalyst. (*b*) Hydrolysis of starches and wood cellulose to yield sugars. Sulphuric, hydrochloric, sulphurous acids as catalysts. (*c*) Hydrolysis of esters using acids (*d*) Hydration of acetylene to yield acetaldehyde. Various acids as catalysts
	Alkalies	(*a*) Hydrolysis as in (*a*) and (*c*) above. NaOH, KOH, $Ca(OH)_2$, MgO, ZnO as catalysts
Dehydration	Acids	(*a*) Manufacture of ether Sulphuric, sulphonic and phosphoric acids as catalysts (*b*) Esterification processes Hydrochloric and sulphuric acids as catalysts
	Oxides	(*a*) Manufacture of ethylene and unsaturated hydrocarbons Clays, Al_2O_3, SiO_2, ThO_2 as catalysts
Halogenation ..	Non-metallic elements	(*a*) Chlorination of carbon disulphide, carbon monoxide and hydrocarbons Carbon, iodine, sulphur as contact agents,
	Chlorides	(*a*) In synthetic organic chemistry $AlCl_3$, $FeCl_3$, $SbCl_5$, $SnCl_4$, $ZnCl_2$, $HgCl_2$, as contact agents

Of catalytic agents other than those recorded in the above tabulation especial mention must be made of the ferments and enzymes (see Rideal and Taylor, Chap. XI) which chiefly promote hydrolytic, oxidation and reduction processes and various processes of coagulation. In the industries these become of importance in the fermentation process of alcohol manufacture and to a lesser degree in acetic acid and acetone manufacture. Enzyme action is paramount in the syntheses of nature.

Radiant energy and, more especially, light are important catalytic agencies not classified in the above. Light plays an important role in processes of halogenation, and in certain oxidation, reduction and condensation reactions; the drying of oils and the various photographic processes may be mentioned in illustration. Cathodic reduction and anodic oxidation are susceptible of catalytic influence and the phenomenon of catalysis intrudes in the electro-chemical phenomena of passivity and over potential.

Promoters.—The admixture of small quantities of other substances with single catalysts, such as are recorded in the preceding section, frequently results in the abnormal increase in catalytic activity of the mixture. Normally, it would be anticipated, the catalytic activity of a mixture should be composite of the several activities of the components and such is of very frequent occurrence. Nevertheless, exceptions are well known and have been freely employed in industrial practice. Thus, in British Pat. No. 27963 of 1913, filed by the Badische Anilin und Soda Fabrik, it is claimed that by admixture of small quantities of chromium and cerium oxides with iron oxide the velocity of the reaction

$$H_2O + CO = CO_2 + H_2$$

can be considerably accelerated. A mixture containing 2.5 per cent Cr_2O_3 and 0.5 per cent CeO_2 operates 700 times more rapidly at 500°C. than does iron oxide alone. To such admixtures the name of catalyst promoters has been given.

The explanation of promoter action is thus far not forthcoming. Indeed, it is probable that no one single theory would be generally applicable. In certain cases, as for example, in the use of molybdenum as a promoter to iron in ammonia synthesis the phenomenon may be associated with the nitride forming or nitrogen adsorbing properties of molybdenum. In cases of carrier action, as, for example, in oxidation

processes, where catalytic action is associated with the tendency of an element to oscillate between two stages of oxidation the function of the promoter may be to increase the temperature range over which the catalytic agent is labile. It would seem, in other cases, that promoters may act by decreasing the sensibility of the catalyst to substances which diminish its activity. Since it is not possible to give any general theory of promoters, nor to lay down any principles to guide the investigator in the choice of promoters, the following tabulation of some of the more important industrial examples has been compiled.

Reaction	Catalyst	Promoters employed or suggested
Contact sulphuric acid process	Burnt pyrites	Oxides of Cu, V, U, Cr, Ni, Co, Al, Be, Zr, Zn, Ce, Th, Di.
Ammonia oxidation	Oxide of iron	Oxides of Cu, Ca, Bi, Ce Cr,
	Platinum	Oxides of Pb, Te,
Deacon chlorine process	Cuprous chloride	Chlorides of several elements
Removal of sulphur compounds from gases	Iron oxides	Oxides of Cr, Ce, Th.
Production of formaldehyde	Various metals	Metallic couples
Oxidation of aniline to aniline black	Copper sulphate or vanadium chloride	p.-diamine or p.-amidophenol
Oxidation of naphthalene.	Mercuric sulphate	Copper sulphate
$CO + H_2O = CO_2 + H_2$.	Iron oxide	Oxides of Cr, Ni, Al, Ce, Th, Zn, Pb, U, Na, Cu, Ag, and Cu metallic couples.
$2CO + H_2$ excess $+ O_2 = 2CO_2 + H_2$ excess	Iron oxide	Oxides of Cr, Ce, Th, La, Al.
Hydrogenation of oils	Reduced nickel	Reduced copper, iron.
Ammonia synthesis	Reduced iron	Reduced Mo, W, Co, Ni, U, Traces of alkalis.

Catalyst Poisons.—Paralleling the abnormal increase in catalytic activity, due to the admixture of small quantities of substances other than the essential catalytic agent, is the abnormal depreciation in activity produced by the presence, in the reacting species, of minute quantities of foreign materials. Such substances are termed catalyst poisons from their analogy with the effect of poisons on the natural processes. It is to the presence of catalyst poisons that much of the earlier ill-success of catalytic processes in industry may be attributed. Thus, the contact process of sulphuric acid manufacture, in presence of finely divided platinum, was patented as early as 1831 (Brit. Pat. No. 6069 of 1831) by Phillips, but the industrial enterprise was not achieved until the beginning of this century, when success had been obtained in the technical production of pure gases. The principal poisons of this catalytic reaction were found to be arsenic, antimony, phosphorus and lead together with suspended solid par-

ticles. Only when such materials were quantitatively removed was technical synthesis possible. Similar observations hold for the various other industrial catalytic processes. Volatile silicon compounds poison the platinum gauze catalyst in ammonia oxidation. Sulphur and chlorine must be rigidly excluded in the catalytic hydrogenation of oil in presence of nickel. Oxides of sulphur and arsenic impair the activity of cuprous chloride in the Deacon chlorine process. Carbon monoxide in the nitrogen-hydrogen mixture for ammonia synthesis, even in concentrations of 0.05 per cent severely reduces the efficiency of the synthetic operation in presence of iron catalysts admixed with promoters while oxygen and water vapor exercise a similar effect. Minute concentrations of sulphur in the reacting gases also destroy the catalytic activity of the medium. It is evident, therefore, that, from the industrial standpoint, the problem of catalyst poisons is of paramount importance.

The most recent and comprehensive discussion of the problem of poisoning in catalysis is due to Bancroft.[1] The literature of the subject is there assembled and in the critical analysis it is concluded that poisons act by decreasing the adsorption of the reacting substances on the catalyst. The selective action of this latter on the materials with which it is brought into contact determines the behavior of the catalyst. Experience shows that the action of a poison varies widely in different cases. Thus, the action may be physical as appears to be the case in ammonia oxidation. The volatile silicon compounds are oxidized on reaching the platinum gauze and are deposited in the form of silica on the strands of the material, thus diminishing the active surface. This is true also of suspended matter in the sulphur gases led to the platinum catalyst in the contact sulphuric acid process. In other cases, as, for example, in the sulphur poisoning of iron catalysts in ammonia synthesis and in processes of preferential combustion, where the poisoning is progressive and cumulative the action appears to be due to chemical reaction between the catalyst and the sulphur gas to form sulphide which is catalytically inert. If the sulphide formed is sufficiently stable to resist reduction the poisoning produced is permanent and can only be removed by oxidation of the sulphide followed by subsequent reduction to the metallic form. A large number of cases are doubtless due to selective adsorption of the poison. This would seem to afford the best explanation of the poisoning influence of carbon monoxide, oxygen and water vapor on iron catalysts for ammonia synthesis. Apparently, even at temperatures of 500 to 600°C. water vapor, resulting from the reduction of carbon monoxide to methane, or from the interaction of hydrogen and oxygen or introduced as such into the reaction gases, is tenaciously held by the reduced metals acting as catalysts and prohibits the exercise of their normal activity. In such cases the poisoning effect is temporary, the original efficiency of the catalyst being gradually restored on passage of the pure gases.

Mechanism of Catalytic Action.—The problem of promoter action is closely allied to the mechanism of the catalytic activity itself. Theories of catalysis may, in the main, be grouped under the two classifications:

(*a*) The intermediate compound theory.
(*b*) The theory of adsorption.

For catalytic reactions in homogeneous system the intermediate compound theory appears to be generally applicable. Thus the data, first put forward by Mrs. Fulhame in 1794 and extended by the researches of Dixon (1880), on

[1] *Jour. Phys. Chem.*, 1917, Vol. **21**, p. 767.

the necessity for the presence of water vapor in the reactions of many gases, for example, in the combination of carbon monoxide and oxygen, can be formulated on the theory that the reactions occur in two stages:

$$2CO + 2H_2O = 2CO_2 + 4H$$
$$4H + O_2 = 2H_2O$$

The fact that sulphuretted hydrogen, ethylene, ammonia, hydrogen chloride and pentane will also facilitate combination of the same two gases seems to support the viewpoint. In the lead chamber process of sulphuric-acid manufacture a similar cycle of reactions is postulated for the reaction mechanism of the catalytic action.

It must be observed, however, that the possibility of heterogeneity even in such apparently homogeneous media as these under discussion, cannot be totally excluded. Under such circumstances the possibility of the second mode of explanation must also be envisaged. In homogeneous liquid systems the intermediate compound theory has been widely accepted since the explanation by Williamson of the function of sulphuric acid in the etherification process previously given. The intermediate compound is employed to explain the large group of catalytic reactions in homogeneous liquid systems in which the active agent is a dilute acid. Thus, in the hydrolysis of esters a recent formulation of the reactions occurring[1] may be represented in the following equilibrium equations:

$CH_3COOC_2H_5 + HCl = CH_3.COOC_2H_5.HCl$ (a binary oxonium compound)
$CH_3COOC_2H_5.HCl + H_2O = CH_3.COO.C_2H_5.HCl.H_2O$ (a ternary oxonium compound)
$CH_3COOC_2H_5.HCl.H_2O = C_2H_5.OH.HCl + CH_3COOH$
$C_2H_5.OH.HCl = C_2H_5OH + HCl.$

Such a representation would account for the observation that the acid accelerates both the hydrolysis and the reverse process of esterification. The proof of the existence of such binary and ternary compounds is given in the systematic researches of Kendall and his colleagues.[2] From these studies the general rule has been deduced that the tendency towards compound formation is the more marked, the greater the chemical contrast between the basic nature of the ester and the acidity of the catalytic agent. The concordance of this conclusion with the observation that the catalytic activity in ester hydrolysis is greatest with the strong acids and diminishes with decreasing strength of acid forms a striking piece of evidence in favor of the intermediate compound theory in such systems.

In heterogeneous catalytic reactions the role of the intermediate compound is less certain. It is apposite, however, to record that catalytic activity is common in the case of substances which may exist in more than one state of oxidation. Cuprous chloride as catalyst in the Deacon chlorine process is an example in point, the reaction mechanism being formulated by the following cycle of equations:

$$2CuCl_2 = Cu_2Cl_2 + Cl_2$$
$$Cu_2Cl_2 + O = CuO.CuCl_2$$
$$CuO.CuCl_2 + 2HCl = 2CuCl_2 + H_2O$$

In support of this is the observation that the chlorides of most substances capable of forming oxychlorides are similarly active in the oxidation of hydrogen chloride to chlorine. Other similar cycles might be cited from industrial catalytic processes, especially in the case of the numerous reactions promoted by the presence of iron

[1] FALK and NELSON, *Jour. Am Chem. Soc.*, 1915, Vol. **37**, p. 1732.
[2] *Jour. Am. Chem. Soc.*, 1914, *et seq.*

oxide. The adsorption theory is however, also a possibility as regards mechanism in the Deacon chlorine process.

Faraday in his researches on the power of metals and other solids to induce the combination of gaseous bodies introduced the physical explanation of catalytic action.[1] According to this theory the phenomena of heterogeneous catalysis are dependent on the exertion of that attractive force possessed by many bodies, . . by which they are drawn into association more or less close, without at the same time undergoing chemical combination though often assuming the condition of adhesion and which occasionally leads, under favorable circumstances, to the combination of solid bodies simultaneously subjected to this attraction. Bodenstein and Fink's researches[2] form strong experimental evidence in support of such a viewpoint, the reaction kinetics being explainable by the assumption that there is an adsorption layer on the surface of the catalyst through which the reactants must pass by diffusion in order to come into contact with the catalyst, where they react practically instantaneously. Bancroft[3] has developed the viewpoint in a comprehensive discussion of contact catalysis, concluding that catalysts tend to produce the system which they adsorb the most strongly. That the catalytic agent accelerates both of the reactions in the equilibrium process must be borne in mind, however, in connection with this expression of viewpoint. The striking researches of Langmuir, in support of his chemical theory of the mechanism of adsorption,[4] supply additional ideas on the nature of the surface layer and consequently on the mechanism of the heterogeneous catalytic reaction. The conclusions reached in investigations of the arrangements of oil films on the surface of water are identical with the conception of contact action which led Twitchell to the development of naphthalene stearo-sulphonic acids as agents for the hydrolytic splitting of fats.[5] Langmuir's views applied to the phenomena of heterogeneous catalysis harmonize to a measured degree the chemical and physical theories of catalytic action. They show that beyond the simple process of adsorption a definite orientation of the molecules may be achieved resulting in an enhanced catalytic activity. Extension of the theory to the explanation of promoter action should doubtless soon be possible.

The Industrial Development of the Catalytic Reaction.—The translation of a given catalytic reaction from the stage of laboratory success to that of the industrial enterprise involves a series of undertakings which, from the nature of the catalytic reaction, are distinctive and peculiar to this type of process. Thus, since catalysis is concerned largely with the velocity with which a process occurs, this property calls for careful consideration. Again, since the catalyst may accelerate reaction over a wide temperature range the equilibrium obtaining in the given process is also of fundamental import since only by a successful combination of the equilibrium factor with the velocity factor may the optimum conditions of reaction be achieved. In a reaction, also, in which the change is localized on the catalytic agent it will be obvious, on consideration, that the thermal magnitudes of the process are of primary importance. The preceding sections which have emphasized the functions of promoter and of poison in modifying the essential catalytic operation serve to indicate further peculiarities inherent in the technical development of the catalytic process.

[1] *Experimental Researches in Electricity*, 1849, Vol **1**, p. 165, 6th series, Nos. 564–659, "Everyman's Library," No. 576, pp. 84–111; *Phil. Trans.*, 1834, Vol **114**, p. 55.

[2] *Zeit. Phys. Chem.*, 1903, 1904, 1905, 1907.

[3] *Jour. Phys. Chem.*, 1917, Vol. **21**, pp. 676, 767.

[4] *Jour. Am. Chem. Soc.*, 1916, Vol. **38**, p. 222, 1917, Vol. **39**, p. 1848, 1918, Vol. **40**.

[5] *Jour. Ind. Eng. Chem.*, 1917, Vol. **9**, p. 194

In exemplification of these factors the historical development of the contact sulphuric acid process may be noted. Discovered by Phillips in 1831 it did not reach large industrial application before the beginning of the present century. In the intervening time, the problems which required solution included the purification of the reacting gases, the preparation of the catalytic medium, the necessary distribution of the catalyst on a suitable support, the determination of the reaction equilibrium to locate the optimum time-temperature conditions of operation and the design of converter units to ensure proper distribution of the reacting substances through the catalytic mass with adequate control of the temperature of the medium. The necessity for the investigation of this last factor arose from the exothermic nature of the reaction between sulphur dioxide and oxygen. The general questions involved in such investigations are set forth in the following pages.

The Equilibrium Data.—For a reversible reaction in which, over the possible range of reaction temperatures, the direction of change may be more or less completely reversed, a prior knowledge of the equilibrium conditions is of the greatest possible advantage. Thus from the equilibrium data of the water-gas reaction previously cited (page 750) it is evident that for the production of a gas with maximum hydrogen or minimum carbon monoxide content at the lowest possible temperature, from water gas and steam, a catalytic agent working at the lowest possible temperature to ensure equilibrium conditions is required. Further, given the minimum working temperature for a suitable catalytic agent at which equilibrium can be attained, a simple calculation from the equilibrium constant determines the ratio of the reactants required to produce a gas of definite concentration of the several reacting species. Thus, in the same example, it has been shown that a steam water-gas ratio of 2 : 1 is adequate for the production of an equilibrium mixture at 500°C. with a carbon monoxide concentration below 2 per cent.

In gas reactions where, from economic causes, there are present in the reaction mixture inert gases operating as diluents, knowledge of the equilibrium data is of especial value. Thus in the contact sulphuric acid process

$$SO_2 + \tfrac{1}{2}O_2 = SO_3$$

the oxygen supplied is diluted with nitrogen from the air. The fractional conversion $x = \frac{[SO_3]}{[SO_3] + [SO_2]}$ can be associated with the equilibrium constant K_p at any temperature and the concentrations a and b are the percentages of sulphur dioxide and oxygen respectively in the initial mixture by means of the equation

$$100x = 100 \frac{K_p}{K_p + \frac{1}{\sqrt{\frac{b - 0.5ax}{100 - 0.5ax}}}}$$

From this equation it may be deduced that, although an increase in the partial pressure of oxygen is beneficial in that it tends to raise the value of x, a limit is set to the quantity of air admitted by the diluent effect of the nitrogen simultaneously introduced. Hence, assuming optimum conditions, namely, a trace of sulphur dioxide and large excess of air, it follows (since $b = 20.9$ per cent) that

$$\sqrt{\frac{b - 0.5ax}{100 - 0.5ax}} \text{ approximates to } \sqrt{\frac{20.9}{100}} = 0.457$$

or correspondingly

$$100x = 100\,\frac{K_p}{K_p + 2.2}$$

Hence, it is only for large values of K_p that the yield approaches theoretical, and K_p is large in this reaction when the temperature is comparatively low; for example, at 450°C., $K_p = 188$. At 700°C. where K_p is only 4.8 it follows that the yield is approximately 60 per cent of the theoretical in spite of the large excess of air assumed to be employed. The economic effect of employing enriched air may also be studied from the same data, since at 700°C. with pure oxygen the value of $100x$ approximates to $\frac{100K_p}{100K_p + 1}$ or 83 per cent. Actually in practice it has been decided that the optimum results are obtained with excess air to raise the oxygen content to the ratio SO_2: $O_2 = 2:3$.[1]

In absence of determinations of the equilibrium data or of facilities for obtaining the same, orientation may be secured into the trend of these by experimental test. Thus, in the hydrogenation of benzene to yield cyclohexane, experimental work of Sabatier showed that hydrogenation occurs freely at 180°C., whereas at 300°C. the reverse process of dehydrogenation of cyclohexane readily occurs in contact with reduced nickel as a catalyst. Obviously within this interval the sign of $\log K_p$ must change. The Nernst approximation formula for equilibrium conditions may often serve as a check on such observations. Thus, in the case cited, the formula has recently been utilized in the author's laboratory with results given below confirming the experimental observations of Sabatier set forth above.

$$C_6H_6 + 3H_2 = C_6H_{12} + 39{,}300 \text{ cal.}$$

According to Nernst's approximation formula

$$\log \frac{pH_2^3\, pC_6H_6}{pC_6H_{12}} = \log K_p = -\frac{39{,}300}{4.571T} + 3(1.75 \log T) + 4.8$$

whence may be obtained the following values:

T°C. =	0	27	200	227	527
$\log K_p$ =	−16.91	−13.85	−1.21	−0.03	8.17

Obviously the hydrogenation of benzene must be conducted at as low a temperature as possible below 227°C. in order to attain maximum hydrogenation in a single passage through the catalyst mass.

The Reaction Velocity.—Given the equilibrium data it is next necessary to obtain comparative data of reaction velocities with different catalysts under fixed conditions of experiment in order to ascertain the most suitable agent to employ. Ordinarily, it is of advantage to make the preliminary measurements with purified reacting species, so that by restriction of the variables the necessary orientation as to relative activities of catalyst may be obtained. In this manner, a norm may be established in terms of which the efficiency of a given catalyst substance may be established. Thus, as the researches of Haber have shown, uranium carbide has been employed in comparing the relative efficiencies of catalysts for ammonia synthesis. Actually, such a catalyst is not employed in technical synthesis owing to its great sensitivity to catalyst poisons. Catalytic agents composed of iron admixed with suitable promoters are preferred to the uranium carbide, although catalytically less efficient, owing to their greater resistivity to traces of foreign gases such as carbon monoxide or sulphur compounds.

[1] (Similar observations on the equilibrium factors in other catalytic reactions may be obtained in RIDEAL and TAYLOR, *loc cit.* pp. 83, 91, 101, 162, 237, 302.)

The measurement of the reaction velocity is relatively simple in the case of homogeneous catalytic reactions, since the concentrations of the several constituents and the course of the reaction can generally be readily ascertained. With heterogeneous reactions the problem is more complex since the several magnitudes required are not capable of precise statement. In illustration of the problem let it be assumed that a given volume of gas or liquid, V, be forced through a bed of granular contact material, v, per unit of time. The ratio V/v may be termed the "space-velocity" ($S.V.$) of the process and is an important magnitude technically since its size determines, in part, the dimensions of the plant required for a given output. In passage through the catalyst space the reaction substances will attain more or less to the

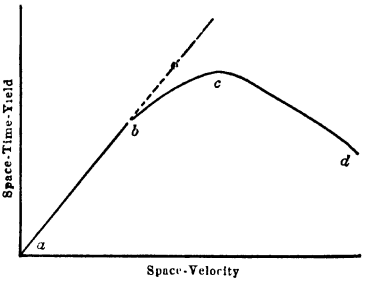


FIG. 1.—Reaction-velocity and yield curve.

equilibrium concentrations according as the rate of passage be slow or rapid. If the fractional conversion of the reacting substances to their equilibrium state be measured it is obvious that this value will decrease as the speed of passage through the mass increases. The product of the fractional conversion R and the space velocity, $S.V.$ will give the space-time yield or the amount of reaction effected in unit time per passage through unit volume of the catalyst space. The variation of the space-time yield with the space velocity will, in general, give a curve of the type shown in the accompanying diagram.

The first branch of the curve ab indicates the region in which the velocity is sufficiently slow for equilibrium conditions to be attained, along the second branch of the curve, bc, the equilibrium is no longer attained, but the deviation from equilibrium concentrations is more than compensated, as regards space-time yield, by the increase in space velocity. On the falling branch of the curve, cd, the space velocity is rising less rapidly than corresponds to the diminution of reaction occurring and so the space-time yield falls away. The curve shows that the optimum conditions of operation do not necessarily coincide with the conditions under which equilibrium is attained at the highest velocity of passage. Higher values of the space velocity and a lower conversion per unit passage may give a greater yield of products per unit of time. For circulatory systems it follows that the point c represents the best conditions of operation, other factors being equal, while with non-circulatory processes the best utilization of the reacting species is attained at b.

Comparison of different catalysts can therefore be expressed in terms of the maximum space-time yield for the different materials for the particular working conditions employed, whether circulatory or non-circulatory. It is to this magnitude that all the variable factors in the catalyst mass, such as influence of temperature, concentration of reactants, purity of materials and life of the catalyst will be referred, the choice of operating material being then decided by adjustment of these data to the economic aspects of the problem.

The Form of the Contact Mass: Catalyst Support Materials.—It is evident that the velocity factor is determined in part by the form of the catalyst material, which also is a factor of considerable importance in the technical catalyst unit. The space velocity has been referred to the volume occupied by the catalyst. The actual velocity of the gas or liquid is determined by the shape, size and distribution of the catalyst mass, which factors also determine the back pressure prevailing in the unit. It has been frequently shown that the catalytic effect is associated with the surface area of the catalyst medium so that, apart from the mechanical difficulties involved, a catalyst bed of finely divided material is preferable. Generally a compromise between the several conflicting items is adopted. The surface factor and the activity of the catalyst are most often greatest when the materials employed are porous and amorphous. If it is impossible to bring the material into such a condition and such a size that the resistance to the passage of the reacting constituents shall not be prohibitively great, the device is adopted of incorporating the catalytic material upon a suitable support.

Thus, in the contact sulphuric acid process the finely divided platinum is employed in several different forms. The original Badische type of plant employed platinized asbestos in long narrow tubular converters. The Tenteleff process exposes the platinum on large coarse asbestos string mats impregnated with platinum black. In the more recent and most successful Grillo-Schroeder contact material, a very active form of platinum black distributed over a large surface is attained by soaking partly dehydrated magnesium sulphate heptahydrate with a spray of a platinum solution the mixture being then ignited in an atmosphere of sulphur dioxide. In this way the platinum is reduced and the salt undergoes further dehydration, puffing up and becoming covered with a thin layer of platinum. The recovery of the catalytic material from such a support is readily accomplished by solution of the magnesium sulphate and flocculation of the metal particles.

Among other supports which have found employment in technical practice mention may be made of pumice, various porous siliceous materials such as fireclay, kieselguhr, alundum and unglazed porcelain, charcoal in its various forms, salts and oxides obtained in a porous condition by ignition and decomposition of suitable raw materials. Granular metallic aluminum is now being used as a thermally conducting support material. As with the catalytic agents, it is impossible to anticipate the particular support which will be found most suitable. In the main, trial and error must be employed to determine this. It follows, however, from considerations set forth in the preceding that care must be exercised to insure that with the support no materials negatively catalytic in nature are introduced. Frequently, in spite of the most patient researches, a suitable catalytic support material cannot be obtained without sacrifice of the maximum efficiency of the catalyst. An adjustment between the several factors must then be made. The ideal support will be a porous material of low density, free from impurities negatively catalytic to the reaction process, itself, if possible, positively catalytic, even though feebly, to the reaction, and as far as possible incapable of reaction with the catalyst mass. With suitable gradation of such a material, the problem of form in the contact material may readily be solved for all sizes of catalyst unit (see Rideal and Taylor, Chap. 3).

Heat of Reaction.—The heat change accompanying a catalytic action determines in large measure the manner of conduct of the process and the design of unit in which to carry out the reaction. Thus, in the catalytic conversion of carbon monoxide and steam to hydrogen and carbon dioxide the reaction is

accompanied by the evolution of 10,000 cal. per gram molecule of reacting carbon monoxide.

$$CO + H_2O = CO_2 + H_2 + 10Kg.\ cal.$$

It may be calculated from specific heat data, and has been demonstrated on a technical unit, that, with a system of heat interchange having a 75 per cent exchange efficiency, this heat evolution is adequate for the maintenance of the reaction temperature, 500°C., without the application of external heat. The steam water-gas mixture in the ratio of 2½ volumes of steam to 1 volume of water gas enters a series of heat interchangers at 100°C., is preheated by the sensible heat of the effluent gases to 450°C., reacts in the catalyst chamber and is thus raised to a temperature somewhat higher than 500°C. and leaves by the heat interchangers in the reverse direction to that of the entering gases, finally passing out at 100°C. With such favorable thermal conditions the process is self sustaining when the heat losses by radiation and conduction do not exceed 25 per cent of the available heat.

With a more energetically exothermic reaction, temperature control becomes a matter of difficulty. Thus, for example, in the contact sulphuric-acid process, the optimum conversion temperature is in the region 400 to 450°C. Should the gases reach the catalyst at that temperature, it follows that with a heat evolution of 21,700 cal. per gram molecule of sulphur dioxide converted, the gases would leave the catalyst at considerably higher temperatures, with correspondingly less efficiency of conversion, due to the equilibrium data. Such complications are avoided in several different ways. In the case under consideration, the Badische converter consisted of narrow reaction tubes permitting high radiation to the incoming gas which passed externally over the tubes in a counter-current direction, the cold gas thus serving to cool the catalyst medium at its hottest part. In the Mannheim process the reaction was conducted in two distinct stages. Energetic reaction was permitted in the first catalyst unit employing burnt pyrites as catalyst at a temperature of 500 to 600°C. In this manner, a 45 per cent conversion was obtained. The gases, after suitable diminution of the temperatures, were led to a platinum-catalyst converter operating at the temperature of maximum efficiency, in which, owing to the lower percentage of sulphur dioxide requiring oxidation, the temperature control was comparatively simple. In other types of contact converters, the sulphur gases are passed over trays of catalyst separated from each other by intervening gas spaces in which the necessary cooling of the gas temperatures may be achieved.

Another device of frequent application to overcome the excessive localization of temperature in gas reactions is the addition of an inert constituent to the gas mixture or the addition in a circulatory process of excess of one of the reacting constituents, or, in a process where the reaction is practically exclusively in one direction, the addition of one of the reaction products to the incoming gases. These devices operate by diminishing the heat evolution per unit volume of total gas, thus lessening the temperature increase of the gas mixture per unit of reaction. Thus, in the removal of 2 per cent of carbon monoxide from hydrogen by processes of preferential combustion with added air or oxygen, the effective temperature range for preference in the combustion process is some 50°C. The thermal effect of the reaction in the simple hydrogen-carbon-monoxide air mixture is adequate in a well-insulated converter to raise the gas temperature at least 150°C., thus destroying the preferential nature of the process. This difficulty has been overcome by admixing steam as an inert constituent, thereby raising the specific heat of the gas mixture per molecule of carbon monoxide requiring oxidation. Similarly in the hydrogenation of acetaldehyde

to yield synthetic alcohol, rigorous temperature control is necessary in order to obviate catalytically accelerated side reactions resulting in the degradation of the aldehyde to methane, carbon monoxide, carbon dioxide and carbon. The exothermic reaction is controlled by employing the hydrogen in large excess in a circulatory process, this having the further advantage that it tends to inhibit the reverse process of dehydrogenation. Finally, the problem of chlorination of hydrocarbons may be cited as an example of reaction in presence of charcoal as catalyst, in which the intensity of the reaction may be minimized by admixing, with the incoming gas, carbon tetrachloride or other saturated chloro-compound. In this way the ready tendency to explosive violence, which this reaction shows, may be restrained.

With reactions which take place with absorption of heat the problems arising in connection with control of catalyst temperature are relatively simple. One or other of the many methods of communicating heat to any reaction system is generally to be found suitable.

SECTION XXIII

COLLOID CHEMISTRY

By Jerome Alexander[1]

Colloid chemistry deals with the properties and behavior of matter in a certain very fine state of subdivision or dispersion, known as the colloidal condition. There are no sharp limitations to the size of colloidal particles; they cover a zone which begins with dimensions somewhat smaller than a wave length of light, and extends downward into the dimensions commonly ascribed to molecules.

The laws of "universal gravitation" do not hold for particles of matter in extremely close proximity. We have but to mention cohesion, adhesion, capillarity, adsorption, and chemical attraction, to call to mind the wide range of practical every-day variations from Newton's law. Molecular attraction necessitated the introduction by van der Waals of the variable a in his well-known gas equation[2]:

$$RT = \left(p + \frac{a}{v_2}\right)\left(v - b\right)$$

With the increasing subdivision of matter into smaller and still smaller particles we begin to enter the zone wherein "molecular" or "physical" forces begin to play an increasingly important part, until they finally become dominant. If the subdivision is profound enough, chemical combination may result. In fact before substances can react chemically, their particles must first be brought into close proximity by solution, fusion, ionization, or even pressure, as was shown by W. Spring, who caused dry powders to unite chemically by extremely high pressures.

No sharp line can, therefore, be drawn between physical and chemical forces; for they seem to blend into each other over the colloidal zone, and to exhibit differences in degree and modification, rather than in lack of common origin. In fact it is readily conceivable that such forces may result from the same ultimate cause as gravitation itself, modified when the structure and motion of the particles cease to be negligible infinitesimals with reference to the distance between the particles. Sir William Thompson has indeed expressed the opinion[3] that it is possible that the phenomena of cohesion and others which are ordinarily ascribed to a departure, at small distances, from the law of gravitation, may not be inconsistent with it.

Coarse powders or suspensions, on the other hand, upon increasing subdivision, pass by insensible gradations into the colloidal zone. About 1827, the English biologist Robert Brown observed that particles approaching in size the limit of microscopic resolvability, 0.1μ, exhibit an oscillatory movement about a mean position, known as the Brownian motion. With the aid of the ultramicroscope, which brings into visibility particles as small as $5\mu\mu$, it can be seen that as the particles become still smaller than 0.1μ, their motion increases enormously in both speed and amplitude, until they exhibit a rapid free-path motion which calculation shows to be a visual,

[1] Pres., Uniform Adhesive Co., Brooklyn, N. Y.

[2] This equation is intended to care for the departures from Boyle's law for gas. The constants a and b for some of the more common gases are given on p 190.

[3] *Proc. Roy. Inst.*, Vol. 11, part III, p. 483.

demonstration of the kinetic theory.[1] By observing an extremely diluted aqueous solution of milk, it can be seen that the Brownian movement of the smallest fat globules seems to be mainly due to swarms of actively moving colloidally dispersed particles of casein, etc., which keep up a ceaseless bombardment from all sides.

From what has just been said, it is obvious that no substance is a colloid, *per se*, but that any substance may be reduced to the colloidal state or condition, providing it is sufficiently subdivided or dispersed. Thus many soaps dissolve in alcohol to form crystalloidally dispersed solutions, whereas their aqueous solutions are colloidal. Sodium chloride, which in water naturally forms a crystalloidal solution, may be colloidally dispersed in benzol.[2]

Although modern investigation has modified some of the notions originally entertained, it is interesting to give a few extracts from the work of Thomas Graham, F. R. S., Master of the Mint. In two basic papers, the first entitled "Liquid Diffusion Applied to Analysis," read before the Royal Society of London, June 13, 1861, the second entitled "On the Properties of Colloidal Silicic Acid and other Analogous Colloidal Substances," published in the *Proceedings of the Royal Society*, June 16, 1864, Graham pointed out the essential facts regarding colloids and the colloidal condition, and established much of the nomenclature now in use. It is remarkable how recent research has confirmed the correctness of most of Graham's views.

"Liquid Diffusion Applied to Analysis."—The property of volatility, possessed in various degrees by so many substances, affords invaluable means of separation, as is seen in the ever-recurring processes of evaporation and distillation. So similar in character to volatility is the diffusive power possessed by all liquid substances, that we may fairly reckon upon a class of analogous analytical resources to arise from it. The range also in the degree of diffusive mobility exhibited by different substances appears to be as wide as the scale of vapor tensions. Thus hydrate of potash may be said to possess double the velocity of diffusion of sulphate of potash, and sulphate of potash again double the velocity of sugar, alcohol, and sulphate of magnesia. But the substances named, belong all, as regards diffusion, to the more "volatile" class. The comparatively "fixed" class, as regards diffusion, is represented by a different order of chemical substances, marked out by the absence of the power to crystallize, which are slow in the extreme. Among the latter are hydrated silicic acid, hydrated alumina, and other metallic peroxides of the aluminous class, when they exist in the soluble form; together with starch, dextrin, and the gums, caramel, tannin, albumen, gelatin, vegetable, and animal extractive matters. Low diffusibility is not the only property which the bodies last enumerated possess in common. They are distinguished by the gelatinous character of their hydrates. Although often largely soluble in water, they are held in solution by a most feeble force. They appear singularly inert in the capacity of acids and bases, and all in the ordinary chemical relations. But, on the other hand, their peculiar physical aggregation with the

[1] Jean Perrin, and The Svedberg. This was clearly forseen by SIR WILLIAM RAMSAY, who in a paper entitled, "Pedetic Motion in Relation to Colloidal Solution" (*Chem News*, Vol **65**, p 90, 1892), stated as follows: " I am disposed to conclude that solution is nothing but subdivision and admixture, owing to attractions between solvent and dissolved substance accompanied by pedetic motion, that the true osmotic pressure has, probably, never been measured, and that a continuous passage can be traced between visible particles in suspension, and matter in solution; that in the words of the old adage, *Natura nihil fit per saltum*."

[2] The elementary definition of a colloid was a substance which would not pass a porous membrane when apparently in solution, while a crystalloid would. This, is of course untrue, and as said again below, Graham himself knew that it was not so.

chemical indifference referred to, appears to be required in substances that can intervene in the organic processes of life. The plastic elements of the animal body are found in this class. As gelatin appears to be its type, it is proposed to designate substances of the class as *colloids*, and to speak of their peculiar form of aggregation as the *colloidal condition of matter*. Opposed to the colloidal is the crystalline condition. Substances affecting the latter form will be classed as *crystalloids*. The distinction is no doubt one of intimate molecular constitution.

"Although chemically inert in the ordinary sense, colloids possess a compensating activity of their own, arising out of their physical properties. While the rigidity of the crystalline structure shuts out external impressions, the softness of the gelatinous colloid partakes of fluidity, and enables the colloid to become a medium for liquid diffusion, like water itself. The same penetrability appears to take the form of cementation in such colloids as can exist at a high temperature, hence a wide sensibility on the part of colloids to external agents. Another and eminently characteristic quality of colloids is their mutability. Their existence is a continued metastasis. A colloid may be compared in this respect to water, while existing liquid at a temperature under its usual freezing-point, or to a supersaturated saline solution. Fluid colloids appear to have always a *pectous* modification and they often pass under the slightest influences from the first into the second condition. The solution of hydrated silicic acid, for instance, is easily obtained in a state of purity, but it cannot be preserved. It may remain fluid for days or weeks in a sealed tube, but is sure to gelatinize and become insoluble at last. Nor does the change of this colloid appear to stop at that point. For the mineral forms of silicic acid, deposited from water, such as flint, are often found to have passed, during the geological ages of their existence, from the vitreous or colloidal into the crystalline condition (H. Rose). The colloidal, is, in fact, a dynamical state of matter; the crystalloidal being the statical condition. The colloid possesses Energia. It may be looked upon as the probable primary source of the force appearing in the phenomena of vitality. To the gradual manner in which colloidal changes take place (for they always demand time as an element), may the characteristic protraction of chemico-organic changes also be referred." (Pp. 183–184.)

"It may perhaps be allowed to me to apply the convenient term *dialysis* to the method of separation by diffusion through a septum of gelatinous matter. The most suitable of all substances for the dialytic septum appears to be the commercial material known as vegetable parchment, or parchment-paper, which was first produced by M. Gaine, and is now successfully manufactured by Messrs. De la Rue." (P. 186.)

"Preparation of Colloid Substances by Dialysis.—The purification of many colloid substances may be effected with great advantage by placing them on the dialyzer. Accompanying crystalloids are eliminated, and the colloid is left behind in a state of purity. The purification of soluble colloids can rarely be effected by any other known means, and dialysis is evidently the appropriate mode of preparing such substances free from crystalloids.

"*Soluble Silicic Acid.*—A solution of silicia is obtained by pouring silicate of soda into diluted hydrochloric acid, the acid being maintained in large excess. But in addition to the hydrochloric acid such a solution contains chloride of sodium, a salt which causes the silicia to gelatinize when the solution is heated, and otherwise modifies its properties. Now such soluble silicia, placed for 24 hr. in a dialyzer of parchment-paper, to the usual depth of 10 mm., was found to lose in that time 5 per cent of its silicic acid and 86 per cent of its hydrochloric acid. After 4 days on the

dialyzer, the liquid ceased to be disturbed by nitrate of silver. All the chlorides were gone, with no further loss of silicia. In another experiment 112 g. of silicate of soda, 67.2 g. of dry hydrochloric acid, and 1,000 c.c. of water were brought together, and the solution placed upon a hoop dialyzer, 10 in. in diameter. After 4 days the solution had increased to 1,235 c.c., by the action of osmose, colloid bodies being generally highly osmotic. The solution now gave no precipitate with nitrate of silver, and contained 60.5 g. of silicia, 6.7 g. of that substance having been lost. The solution contained 4.9 per cent of silicic acid.

"The pure solution of silicic acid so obtained may be boiled in a flask and considerably concentrated, without change; but when heated in an open vessel a ring of insoluble silica is apt to form round the margin of the liquid, and soon causes the whole to gelatinize. The pure solution of hydrated silicic acid is limpid and colorless, and not in the least degree viscous, even with 14 per cent of silicic acid. The solution is the more durable the longer it has been dialyzed and the purer it is. But this solution is not easily preserved beyond a few days, unless considerably diluted. It soon appears slightly opalescent, and after a time the whole becomes pectous somewhat rapidly, forming a solid jelly, transparent and colorless, or slightly opalescent and no longer soluble in water. This jelly undergoes a contraction after a few days, even in a close vessel, and pure water separates from it. The coagulation of the silicic acid is effected in a few minutes by a solution containing $\frac{1}{10,000}$ part of any alkaline or earthy carbonate, but not by caustic ammonia, nor by neutral or acid salts. Sulphuric, nitric and acetic acids do not coagulate silicic acid, but a few bubbles of carbonic acid passed through the solution produce that effect after the lapse of a certain time. Alcohol and sugar, in large quantity even, do not act as precipitants; but neither do they protect silicic acid from the action of alkaline carbonates, nor from the effect of time in pectinizing the fluid colloid. Hydrochloric acid gives stability to the solution; so does a small addition of caustic potash or soda.

"This pure water-glass is precipitated on the surface of a calcareous stone without penetrating, apparently from the coagulating action of soluble lime-salts. The hydrated silicic acid then forms a varnish, which is apt to scale off on drying. The solution of hydrated silicic acid has an acid reaction somewhat greater than that of carbonic acid. It appears to be really tasteless (like most colloids) although it occasions a disagreeable persistent sensation in the mouth after a time, probably from precipitation.

"Soluble hydrated silicic acid, when dried in the air-pump receiver, at 15°, formed a transparent glassy mass of great luster, which was no longer soluble in water. It retained 21.99 per cent of water after being kept 2 days over sulphuric acid.

"The colloidal solution of silicic acid is precipitated by certain other soluble colloids, such as gelatin, alumina, and peroxid of iron, but not by gum nor caramel. As hydrated silicic acid, after once gelatinizing, cannot be made soluble again by either water or acids, it appears necessary to admit the existence of two allotropic modifications of that substance, namely, soluble hydrated silicic acid, and insoluble hydrated silicic acid, the fluid and pectous forms of this colloid." (Pp. 204–205.)

"The possession of a soluble and an insoluble (fluid and pectous) modification is not confined to hydrated silicic acid and the aluminous oxids, but appears to be very general, if not universal, among colloid substances. The double form is typified in the fibrin of blood." (Pp. 212, 213.)

"The separation of colloids from crystalloids by dialysis is, in consequence, generally more complete than might be expected from the relative diffusibility of the two classes of substances." (P. 214.)

"Colloidal Condition of Matter."—I may be allowed to advert again to the radical distinction assumed in this paper to exist between colloids and crystalloids in

their intimate molecular constitution. Every physical and chemical property is characteristically modified in each class. They appear like different worlds of matter, and give occasion to a corresponding division of chemical science. The distinction between these kinds of matter is that subsisting between the material of a mineral and the material of an organized mass.

"The colloidal character is not obliterated by liquefaction, and is therefore more than a modification of the physical condition of solids. Some colloids are soluble in water, as gelatin and gum arabic; and some are insoluble like gum tragacanth. Some colloids, again, form solid compounds with water, as gelatin and gum tragacanth, while others, like tannin, do not. In such points the colloids exhibit as great a diversity of property as the crystalloids. A certain parallelism is maintained between the two classes, notwithstanding their differences.

"The phenomena of the solution of a salt or crystalloid probably all appear in the solution of a colloid, but greatly reduced in degree. The process becomes slow; time, indeed, appearing essential to all colloidal changes. The change of temperature, usually occurring in the act of solution, becomes barely perceptible. The liquid is always sensibly gummy or viscous when concentrated. The colloid, although often dissolved in a large proportion by its solvent, is held in solution by a singularly feeble force. Hence colloids are generally displaced and precipitated by the addition to their solution of any substance from the other class. Of all the properties of liquid colloids, their slow diffusion in water, and their arrest by colloidal septa, are the most serviceable in distinguishing them from crystalloids. Colloids have feeble chemical reactions, but they exhibit at the same time a very general sensibility to liquid reagents as has already been explained.

"While soluble crystalloids are always highly sapid, soluble colloids are singularly insipid. It may be questioned whether a colloid, when tasted, ever reaches the sentient extremities of the nerves of the palate, as the latter are probably protected by a colloidal membrane, impermeable to soluble substances of the same physical constitution." (P. 220.)

"A tendency to spontaneous change, which is observed occasionally in crystalloids, appears to be general in the other class. The fluid colloid becomes pectous and insoluble by contact with certain other substances, without combining with these substances, and often under the influence of time alone. The pectizing substance appears to hasten merely an impending change. Even while fluid a colloid may alter sensibly, from colorless becoming opalescent; and while pectous the degree of hydration may become reduced from internal change. The gradual progress of alteration in the colloid effected by the agency of time, is an investigation yet to be entered upon.

"The equivalent of a colloid appears to be always high, although the ratio between the elements of the substances may be simple. Gummic acid, for instance, may be represented by $C_{12}H_{11}O_{11}$, but judging from the small proportions of lime and potash which suffice to neutralize this acid, the true numbers of its formula must be several times greater. It is difficult to avoid associating the inertness of colloids with their high equivalents, particularly where the high number appears to be attained by the repetition of a smaller number. The inquiry suggests itself whether the colloid molecule may not be constituted by the grouping together of a number of smaller crystalloid molecules, and whether the basis of colloidality may not really be this composite character of the molecule.

"With silicic acid, which can exist in combination both as a crystalloid and colloid, we have two series of compounds, silicates and cosilicates, the acid of the latter appearing to have an equivalent much greater (36 times greater in one salt) than the acid in a variety of metallic salts, such as certain red salts of iron, is accounted

for by the high colloidal equivalent of their bases. The effect of such an insoluble colloid as Prussian blue in carrying down small proportions of the precipitating salts, may admit of a similar explanation. (P. 221.)

"The hardness of the crystalloid, with its crystalline planes and angles, is replaced in the colloid by a degree of softness, with a more or less rounded outline. The water of crystallization is represented by the water of gelatination. The water in gelatinous hydrates is aptly described by M. Chevreul as retained by 'capillary affinity,' that is, by an attraction partaking both of the physical and chemical character." (P. 222.)

"On the Properties of Silicic Acid and Other Analogous Colloidal Substances.— The prevalent notions respecting solubility have been derived chiefly from observations on crystalline salts, and are very imperfectly applicable to the class of colloidal substances. Hydrated silicic acid, for instance, when in the soluble condition, is, properly speaking a liquid body, like alcohol, miscible with water in all proportions. We have no degrees of solubility to speak of with respect to silicic acid, like the degrees of solubility of a salt, unless it be with reference to silicic acid in the gelatinous condition, which is usually looked upon as destitute of solubility. The jelly of silicic acid may be more or less rich in combined water, as it is first prepared, and it appears to be soluble in proportion to the extent of its hydration. A jelly containing 1 per cent of silicic acid, gives with cold water a solution containing about 1 of silicic acid in 5,000 water; a jelly containing about 5 per cent of silicic acid gives a solution containing about 1 part of acid in 10,000 water. A less hydrated jelly than the last mentioned is still less soluble; and finally, when the jelly is rendered anhydrous, it gives gummy-looking, white masses, which appear to be absolutely insoluble, like the light dusty silicic acid obtained by drying a jelly charged with salts, in the ordinary analysis of a silicate.

"The liquidity of silicic acid is only affected by a change, which is permanent (namely, coagulation or pectization), by which the acid is converted into the gelatinous or pectous form, and loses its miscibility with water. The liquidity is permanent in proportion to the degree of dilution of silicic acid, and appears to be favored by a low temperature. It is opposed, on the contrary, by concentration, and by elevation of temperature. A liquid silicic acid of 10 or 12 per cent pectizes spontaneously in a few hours at the ordinary temperature, and immediately when heated. A liquid of 5 per cent may be preserved for 5 or 6 days; a liquid of 2 per cent for 2 or 3 months; and a liquid of 1 per cent has not pectized after 2 years. Dilute solutions of 0.1 per cent or less are no doubt practically unalterable by time and hence the possibility of soluble silicic acid existing in nature. I may add, however, that no solution, weak or strong, of silicic acid in water has shown any disposition to deposit *crystals*, but always appears on drying as a colloidal glassy hyalite. The formation of quartz crystals at a low temperature, of so frequent occurrence in nature, remains still a mystery. I can only imagine that such crystals are formed at an inconceivably slow rate and from solutions of silicic acid which are extremely dilute. Dilution no doubt weakens the colloidal character of substances, and may therefore allow their crystallizing tendency to gain ground and develop itself, particularly where the crystal once formed is completely insoluble, as with quartz.

"The pectization of liquid silicic acid is expedited by contact with solid matter in the form of powder. By contact with pounded graphite, which is chemically inactive, the pectization of a 5 per cent silicic acid is brought about in an hour or two, and that of a 2 per cent silicic acid in 2 days. A rise of temperature of 1.1°C. was observed during the formation of the 5 per cent jelly.

"The ultimate pectization of silicic acid is preceded by a gradual thickening in the liquid itself. The flow of liquid colloids through a capillary tube is always slow compared with the flow of crystalloid solutions, so that a liquid-transpiration-tube may be employed as a colloidoscope. With a colloid liquid alterable in viscosity, such as silicic acid, the increased resistance to passage through the colloidoscope is obvious from day to day. Just before gelatinizing, silicic acid flows like an oil.

"A dominating quality of colloids is the tendency of their particles to adhere, aggregate, and contract. This idio-attraction is obvious in the gradual thickening of the liquid, and when it advances leads to pectization. In the jelly itself, the specific contraction in question, or synaeresis, still proceeds, causing separation of water, with the division into a clot and serum; and ending in the production of a hard stony mass, of vitreous structure, which may be anhydrous, or nearly so, when the water is allowed to escape by evaporation. The intense synaeresis of isinglass dried in a glass dish over sulphuric acid *in vacuo* enables the contracting gelatin to tear up the surface of the glass. Glass itself is a colloid, and the adhesion of colloid to colloid appears to be more powerful than that of colloid to crystalloid. The gelatin, when dried in the manner described upon plates of calcspar and mica, did not adhere to the crystalline surface, but detached itself on drying. Polished plates of glass must not be left in contact, as is well known, owing to the risk of permanent adhesion between their surfaces. The adhesion of broken masses of glacial phosphoric acid to each other is an old illustration of colloidal synaeresis.

"Bearing in mind that the colloidal phasis of matter is the result of a peculiar attraction and aggregation of molecules, properties never entirely absent from matter, but more greatly developed in some substances than in others, it is not surprising that colloidal characters spread on both sides into the liquid and solid conditions." (Pp. 335, 336.)

Graham goes on to say that certain fluid substances which exercise no pectizing influence on colloids, can totally or partially displace the combined water of colloidal silicic acid, without causing the coagulation of the colloid. Hydrochloric, nitric, acetic, and tartaric acids, sugar syrup, glycerin, and alcohol are in this class. He then describes the production of such a solution of silicic acid in alcohol and the *alcogel*.

"The *alcogel*, or solid compound, is readily prepared by placing masses of gelatinous silicic acid, containing 8 or 10 per cent of the dry acid, in absolute alcohol, and changing the latter repeatedly till the water of the hydrogel is fully replaced by alcohol. The alcogel is generally slightly opalescent, and is similar in aspect to the hydrogel, preserving very nearly its original bulk. The following is the composition of an alcogel carefully prepared from a hydrogel which contained 9.33 per cent of silicic acid.

Alcohol	88.13
Water	0.23
Silicic acid	11.64
	100.00

"Placed in water, the alcogel is gradually decomposed—alcohol diffusing out and water entering instead, so that a hydrogel is reproduced. (Pp. 337, 338.)

"The compound of sulphuric acid, *sulphagel*, is also interesting from the facility of its formation, and the complete manner in which the water of the original hydrogel is removed. A mass of hydrated silicic acid may be preserved unbroken if it is first placed in sulphuric acid diluted with two or three volumes of water, and then transferred gradually to stronger acids, till at last it is placed in concentrated oil of vitriol. The sulphagel sinks in the latter fluid, and may be distilled with an excess

of it for hours without losing its transparency or gelatinous character. It is always somewhat less in bulk than the primary hydrogel, but not more, to the eye, than one-fifth or one-sixth part of the original volume. This sulphagel is transparent and colorless. When a sulphagel is heated strongly in an open vessel, the last portions of the monohydrated sulphuric acid in combination are found to require a higher temperature for their expulsion than the boiling-point of the acid. The whole silicic acid remains behind, forming a white, opaque, porous mass, like pumice. A sulphagel placed in water is soon decomposed, and the original hydrogel reproduced. No permanent compound of sulphuric and silicic acids, of the nature of a salt, appears to be formed in any circumstances. A sulphagel placed in alcohol gives ultimately a pure alcogel. Similar jellies of silicic acid may readily be formed with the monohydrates of nitric, acetic, and formic acids, and are all perfectly transparent.

"The production of the compounds of silicic acid now described indicates the possession of a wider range of affinity by a colloid than could well be anticipated. The organic colloids are no doubt invested with similar wide powers of combination, which may become of interest to the physiologist. The capacity of a mass of gelatinous silicic acid to assume alcohol, or even olein, in the place of water of combination, without disintegration or alteration of form, may perhaps afford a clue to the penetration of the albuminous matter of membrance by fatty and other insoluble bodies, which seems to occur in the digestion of food. Still more remarkable and suggestive are the *fluid* compounds of silicic acid. The fluid alcohol or olein compound favors the possibility of the existence of a compound of the colloid albumen with olein, soluble also and capable of circulating with the blood.

"The feebleness of the force which holds together two substances belonging to different physical classes, one being a colloid and the other a crystalloid, is a subject deserving notice. When such a compound is placed in a fluid the superior diffusive energy of the crystalloid may cause its separation from the colloid. Thus, of hydrated silicic acid, the combined water (a crystalloid) leaves the acid (a colloid) to diffuse into alcohol; and if the alcohol be repeatedly changed, the entire water is thus removed alcohol (another crystalloid) at the same time taking the place of water in the combi,nation with the silicic acid. The liquid in excess (here the alcohol) gains entire possession of the silicic acid. The process is reversed if an alcogel be placed in a considerable volume of water. Then alcohol separates from combination, in consequence of the opportunity it possesses to diffuse into water; and water, which is now the liquid present in excess, recovers possession of the silicic acid. Such changes illustrate the predominating influence of mass.

"Even the compounds of silicic acid with alkalies yield to the decomposing force of diffusion. The compound of silicic acid with 1 or 2 per cent of soda is a colloidal solution, and, when placed in a dialyzer over water *in vacuo* to exclude carbonic acid, suffers gradual decomposition. The soda diffuses off slowly in the caustic state, and gives the usual brown oxide of silver when tested with the nitrate of that base."

Many other colloids are dealt with by Graham in these two papers, including gum, dextrin, caramel, albumen, alumina; stannic, tungstic, titanic and molybdic acids, etc. Contrary to what is commonly believed, Graham was fully aware that colloids dialyze to some extent. Thus he expressly states that sodium chloride dialyzes about 200 times faster than tannic acid, about 400 times faster than gum arabic, and about 1,000 times faster than pure albumen prepared according to the method of Wurtz.

Classification of Colloids.—Since a colloid results from the subdivision, within limits, of a substance in a medium, the broadest classification of colloids is that proposed by Wolfgang Ostwald[1] who grouped them according to the physical

[1] *Kolloid Zeit.*, Vol. 1, p. 291.

state (gaseous, liquid or solid) of the subdivided substance (dispersed phase), and of the medium in which the particles are distributed (dispersion medium). Table 1 shows the nine groups, and gives some instances of each.

TABLE 1

Disperse phase	Dispersion medium	Example
Gas	Gas	No example since gases are miscible in all proportions.
Gas	Liquid	Fine foam, gas in beer.
Gas	Solid	Gaseous inclusions in minerals (meerschaum, pumice), hydrogen in iron, oxygen in silver.
Liquid	Gas	Atmospheric fog, clouds, gases at critical state.
Liquid	Liquid	Emulsions of oil in water, cream; colloidal water in chloroform.
Liquid	Solid	Mercury in ointments, water in paraffin wax. Liquid inclusions in minerals.
Solid	Gas	Cosmic dust, smoke, condensing vapors (ammonium chloride).
Solid	Liquid	Colloidal gold, colloidal sodium chloride, colloidal ice in chloroform.
Solid	Solid	Solid solutions, colloidal gold in ruby glass, coloring matter in gems.

This classification is more theoretical than practical, for the properties of colloids are dependent mainly upon the specific nature of the dispersed substance, its degree of subdivision, and the presence of other substances, which though present in minimal quantities may produce potent stabilizing or coagulative effects. It is not possible to classify colloids according to the size of the dispersed phase, because most colloidal solutions contain particles of different sizes.

The most acceptable classification is that suggested by Hardy[1] and further developed by Zsigmondy, whereby colloids are divided into two broad classes, depending upon their behavior upon dessication at ordinary temperatures—the reversible colloids which redissolve, and the irreversible colloids which do not. This classification is illustrated by Table 2, taken from Zsigmondy,[2] which gives some instances of each group. The varying stretch of the names over the horizontal lines, which indicate dimensions, corresponds to the approximate size-limits of the dispersed particles in each substance.

It is interesting to note that the addition of a little reversible colloid, may render an irreversible colloid reversible (protective action). Furthermore no sharp line is to be drawn between reversible and irreversible colloids, for besides intermediate or transition cases between the two classes, there may be recognized two groups of irreversible colloids, roughly defined by their behavior upon concentration: (1) The completely irreversible, which coagulate while still quite dilute and separate sharply from the solvent with the formation of a pulverulent precipitate, rather than a gel (*i.e.*, pure colloidal metals). Chemical or electrical energy is needed to bring them back again into colloidal solution. (2) The incompletely reversible, which when quite

[1] *Proc. Roy. Soc.*, Vol. 66, p. 95, (1900).
[2] "Coloids and the Ultramicroscope," J. WILEY and SONS, p. 26.

TABLE 2

0.1$\mu\mu$	1$\mu\mu$	10$\mu\mu$	100$\mu\mu$	1μ	10μ	100μ	1mm.
Ultramicroscopic field				Microscopic field, Real forms of particles may be seen			
Quartz in solution does not form a sediment				Quartz solution forms a sediment			
Oil emulsions in water do not separate into two layers				Oil emulsions in water separate into two layers			
Particles pass through filter paper				Particles may be filtered out			
Very rapid Brownian movement				Slow		None	
Crystalloidal solutions	Hydrosols colloidal solutions		Turbidities	Suspensions			

TABLE 2A

REVERSIBLE HYDROSOLS	IRREVERSIBLE HYDROSOLS
Lea's colloidal silver	Colloidal metals (usually)
Colloidal indigo	Bredig's colloidal gold
Paal's blue colloidal gold	Colloidal sulphides
Glycogen solution	Many colloidal sulphides
Soluble starch	Purple of Cassius
Crystallized albumen	
Dextrin	
Molybdic acid	

concentrated, form a gel which may be easily redissolved or peptisized by comparatively small amounts of reagents, unless the evaporation has proceeded too far (*i.e.*, colloidal stannic acid).

Size of Colloidal Particles.—In order to give some idea as to the size of colloidal particles as compared with other dimensions of the same order, the table on p. 775 has been prepared.

The size of colloidal particles may be determined with the aid of the ultramicroscope, by counting the number of particles in a definite volume of a highly diluted colloidal solution of known concentration, or by measuring the mean distance between the particles.[1]

Let d = average diameter of particles,
s = specific gravity of dispersed substances,
a = mass of dispersed substance,
n = number of particles, and
r = mean distance between particles.

[1] SIEDENTOPF and ZSIGMONDY, "Drude's Annual," Vol. 10, p. 30–39, 1903. ZSIGMONDY, "Colloids and the Ultramicroscope," p. 117.

Then in the first case

$$d = \sqrt[3]{\frac{A}{s \cdot n}}$$

And in the second case

$$d = \sqrt[3]{\frac{A \cdot r}{s}}$$

These formulas are based on the assumption that all the particles of the dispersed substance are actually counted, a condition which is practically never realized. Some particles are amicroscopic (*i.e.*, too small to be seen in the ultramicroscope); some may be reduced to molecular dispersion; and even at the high illumination at which the counts should be made, there is the possibility of the superior brilliancy of large particles obscuring the presence of smaller ones. The error thus introduced does not exceed 20 per cent, and is usually considerably less.

TABLE 3

0.1$\mu\mu$	Theoretical size of hydrogen molecule.
0.5$\mu\mu$	Theoretical size of methyl alcohol molecule.
0.8$\mu\mu$	Theoretical size of chloroform molecule.
1—0.02$\mu\mu$	Thickness of electrical double layer.
1.7$\mu\mu$	Size of small particles in colloidal gold solutions.
3—1$\mu\mu$	Thickness of metal films which polarize platinum.
4—3$\mu\mu$	Mean distance between centers of nearest molecules in gases at 760 mm. and 0°C.
5$\mu\mu$	Approximate size of molecule of soluble starch.
	Approximate limit of ultramicroscopic visibility of individual particles in colloids.
10—5$\mu\mu$	Thickness of permanent water film on glass at 23°C.
12$\mu\mu$	Thickness of black soap films.
	Action of silver plate on phase of reflected light alters.
	Range of unstable thickness ends.
40$\mu\mu$	Wave length of mean violet light.
50$\mu\mu$	Wave length of mean green light.
60$\mu\mu$	Wave length of mean red light.
50$\mu\mu$	Approximate value of ρ, the radius of molecular attraction.
60$\mu\mu$	Gold hydrosols having this average particle size are unstable.
75$\mu\mu$	Gold particles settle out.
96—45$\mu\mu$	Range of unstable thickness begins.
90$\mu\mu$	Thickness of gold leaf.
100$\mu\mu$	Approximate lower limit of size of particles in suspensions.
150$\mu\mu$	Limit of resolving power of microscope objective of 1.4 numerical aperture.
500—2,000$\mu\mu$ (0.5—2μ)	Diameter of various spherical bacteria (cocci).
4,000—15,000$\mu\mu$ (4—15μ)	Length of anthrax bacillus (width about 1,000$\mu\mu$).

The size of colloidal particles may also be estimated by means of ultrafiltration. An ultrafilter is essentially a layer of a jelly properly supported, through which a colloidal solution may be forced by appropriate pressure. By using jellies of different kinds and concentrations, and layers of varying thickness, ultrafilters may be prepared having varying degrees of permeability to colloidal particles. Four methods of gauging ultrafilters are given by Bechhold,[1] who also prepared the following table

[1] "Colloids in Biology and Medicine" (trans. by Bullowa) D. Van Nostrand Co., p. 99.

(Table 4) showing the relative sizes in decreasing order of size of the particles of various colloids, as determined by using ultrafilters of different degrees of porosity.

TABLE 4

Suspensions	
Prussian blue	Hemoglobin solution, 1 per cent molecular weight about 16,000
Platinum hydrosol (Bredig)	Serum albumin, molecular weight 5,000 to 15,000
Ferric oxide hydrosol	Diphtheria toxin
Casein, in milk	Protalbumoses
Arsenic sulphide hydrosol	Colloidal silicic acid
Gold hydrosol No. 4 (Zsigmondy) about $40\mu\mu$	Lysalbinic acid
Bismon, colloidal bismuth oxide (Paal)	Deuteroalbumose *A*
	Deuteroalbumose *B*, molecular weight about 2,400
Lysargin, colloidal silver (Paal)	Deuteroalbumose *C*
Collargol, colloidal silver von Heyden, $20\mu\mu$	Litmus
Gold hydrosol No. 0 (Zsigmondy) about 1 to 4 $\mu\mu$	Dextrin, molecular weight about 965.
Gelatin solution, 1 per cent	*Crystalloids*

The Ultramicroscope.—Since this instrument revolutionized colloid research, a brief description of it is essential. A discussion of the scientific principles involved in ultramicroscopy together with the prior history of microscopy leading to its development are given by E. F. Burton.[1]

The ultramicroscope consists essentially of a compound microscope arranged so as to examine against a black background (dark field), objects powerfully illuminated by an intense beam of light at right angles (or approximately at right angles) to the optical axis of the microscope. If a particle diffracts sufficient light to affect the retina, it becomes visible against the dark background, just as the motes in the air become visible when a sun beam enters a dark room. The efficiency of the instrument depends upon the intensity of the illuminating beam and the elimination of extraneous light from the dark field.

Just as in the cosmic field even the most powerful telescope fails to resolve the fixed stars, which are nevertheless visible as points of light, so too in the ultramicroscopic field tiny colloidal particles are *visible*, although we may never hope to *resolve* them, since they are smaller than a wave length of light itself. The limits of visibility of particles in the ultramiscroscope depend upon (1) the specific light-reflecting capacity of the particles, (2) their difference in refractive index from that of the medium surrounding them, (3) the intensity of the illuminating beam, (4) the darkness of the field. Large particles in the field, because of their superior luminosity, obscure the presence of smaller ultramicrons, just as the full moon renders the smaller stars invisible to the naked eye. If too large a number of small particles is present there results only an illuminated field—a miniature Milky Way.[6] Particles below microscopic range, but visible in the ultramicroscope are called *ultramicrons;* particles invisible even in the ultramicroscope are called *amicrons.* Dyes like uranin, fluorescin and eosin, even in extremely dilute solution, show an illuminated field, which may

[1] "The Physical Properties of Colloidal Solutions." Longmans, Green and Co., 1916. See also "Colloids and the Ultramicroscope."

be apparently due to a large number of amicroscopic particles, although it is commonly ascribed to fluorescence.

Preparation of Colloidal Solutions.—Some substances are inherently colloidal (gelatin, gum arabic, egg albumen) and readily yield hydrosols on being dissolved in water. As Svedberg has observed the other methods of preparing colloidal solutions fall naturally into two classes: (1) *condensation methods*, whereby the colloidal state is reached by the aggregation or building up of molecularly dispersed particles to colloidal dimensions; (2) *dispersion methods*, whereby larger particles are reduced down to colloidal state. A few instances of each class will be given.

Condensation Methods.—(*a*) *Colloidal Gold Hydrosol* (Faraday, Zsigmondy). Dissolve 15 mg. of gold hydrochloride ($AuHCl_4.3H_2O$) and 37 mg. of the purest potassium carbonate in 120 c.c. of conductivity water (re-distilled through a silver worm). Then add 0.5 c.c. of an ethereal solution of yellow phosphorus, made by diluting a concentrated solution with five times its volume of ether. The hydrosol forms slowly, passing through a yellowish-brown to a bright ruby-red. Traces of impurities found in ordinary distilled water, especially alkaline earth phosphates, silicates, etc., are apt to mar the results, and lead to the formation of bluish or violet suspensions of gold, which settle out. Ordinary tap water will yield fair results, however, if there first be added to it a few drops of a good protector, such as warm gelatin solution or gum arabic. In this case the potassium carbonate may be dispensed with.

(*b*) *Colloidal Arsenious Sulphide.*—This is readily prepared by running a solution of arsenious acid into sulphuretted hydrogen water, kept saturated by a stream of the gas.

(*c*) *Colloidal Resins, Oils, etc.*—These may be first reduced to crystalloidal dispersion by solution in alcohol, and the alcoholic solution diluted with water sufficiently to cause aggregation to colloidal dimensions. Thus alcoholic mastic solution when diluted yields a colloidal dispersion. In preparing perfumed alcohol for shaving, it is usual to make a solution of essential oils in alcohol, which upon proper dilution with water, gives a cloudy but stable colloidal emulsion.

Dispersion Methods.—(*a*) By prolonged grinding or agitation, especially in the presence of protective or deflocculating substances, many substances become reduced, in part at least, to the colloidal state. The grinding of ultramarine and of ores, the preparation of Chinese or india ink, the homogenizing of milk, and the "freeing out" of clay, may be mentioned as examples.

(*b*) *Electrical Atomization.*—Bredig[1] first applied this method to the manufacture of stable colloidal solutions of metals. He caused an electric arc (current 4 to 10 amp., potential difference at arc 30 to 100 volts) to pass between electrodes of chemically pure metals, below the surface of distilled water contained in a clean vessel of very insoluble glass or porcelain. It is essential that there be no mixture of electropositive and electronegative metals in the electrodes, and an intermittent sparking of the arc produced by a mechanically operated circuit breaker is desirable. By the use of oscillating discharges at from 30 to 200 volts from an induction coil, Svedberg reduced the current density to a fraction of that required by Bredig (from 1 or 2 amp. down to about 10 mil-amp.); and he was thus enabled to produce a large number of hydrosols and organosols.

(*c*) *Chemical Dispersion.*—Many precipitates may be brought into colloidal dispersion by the addition of small quantities of proper reagents which may then be

[1] BREDIG—"Anorganische Fermente." Faraday had previously used the electric arc to produce finely dispersed gold.

dialyzed out; ferric hydroxide by small quantities of ferric chloride or hydrochloric acid, copper ferrocyanide by ammonium oxalate.

I cannot do better than to quote here the pregnant words of Graham: "The pectization of liquid silicic acid and many other liquid colloids is effected by contact with minute quantities of salts in a way which is not understood. On the other hand, the gelatinous acid may again be liquefied, and have its energy restored by contact with a very moderate amount of alkali. The latter change is gradual, 1 part of caustic soda, dissolved in 10,000 water, liquefying 200 parts of silicic acid (estimated dry) in 60 min. at 100°C. Gelatinous stannic acid is also easily liquefied by a small proportion of alkali, even at ordinary temperature. The alkali, too, after liquefying the gelatinous colloid, may be separated again from it by diffusion into water upon a dialyzer. The solution of these colloids, in such circumstances, may be looked upon as analogous to the solution of insoluble organic colloids witnessed in animal digestion, with the difference that the solvent fluid here is not acid, but alkaline. Liquid silicic acid may be represented as the 'peptone' of gelatinous silicic acid; and the liquefaction of the latter by a trace of alkali may be spoken of as the peptization of the jelly. The pure jellies of alumina, peroxide of iron, and titanic acid, prepared by dialysis, are assimilated more closely to albumen, being peptized by minute quantities of hydrochloric acid."

Consequences of Subdivision.—The most striking results of the subdivision of a substance to colloidal dimensions, follow from the enormous development of free surface. Table 5, adapted from Wo. Ostwald, shows the interfacial development resulting from the progressive decimal subdivision of a cube.

TABLE 5.—RESULTS OF THE PROGRESSIVE DECIMAL SUBDIVISION OF A CUBE

Length of edge	Number of cubes	Total surface
1.0 cm.	1	6 sq. cm. or 0 93 sq. in.
1 0 mm.	10^3	60 sq. cm. or 9.3 sq. in.
0 1 mm.	10^6	600 sq. cm. or 93.0 sq. in.
0.01 mm.	10^9	6,000 sq. cm. or 6.46 sq. ft.
1.0 μ	10^{12}	6 sq. m. or 64 6 sq. ft.
0 1 μ	10^{15}	60 sq. m. or 645 97 sq. ft.
0.01 μ	10^{18}	600 sq. m. or 6,459.72 sq. ft.
1.0 $\mu\mu$	10^{21}	6,000 sq. m. or 1 48 acres
0 1 $\mu\mu$	10^{24}	6 hectares or 14 83 acres
0.01 $\mu\mu$	10^{27}	60 hectares or 148.3 acres
0.001 $\mu\mu$	10^{30}	6 sq. km. or 2 32 sq. mi.

From this it is obvious that surface forces such as surface tension, adsorption, capillarity, and even chemical attraction become enormously magnified and of transcendent importance. Thus colloidal sulphur reduces silver salts energetically, whereas even fine precipitated sulphur does not form silver sulphide in the cold, and does so only partially upon boiling.

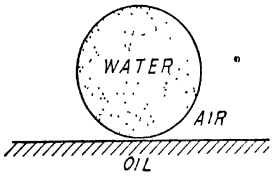


FIG. 1.

Surface Tension.—Figure 1 represents a droplet of water on an oiled surface. Omitting from consideration such disturbing factors as gravitation, evaporation, etc., the following main forces are at work: (1) the attraction of the water molecules for each other;

(2) the attraction between the air and the water; (3) the attraction between the air and the oiled surface; (4) the attraction between the water and the oiled surface.

Regarding for the moment only the water and the air, the attraction of the water molecules for each other tends to make the droplet assume the shape exposing a minimum surface, *i.e.*, a sphere. In considering this sphere, it is evident that the molecules on its surface occupy an anomalous position; they are attracted inwardly by the relatively strong attraction of the interior water molecules, and outwardly by the relatively weak attraction of the air. The residual attraction in the surface layer results in the formation of a surface skin, and the strength of this surface film is called the surface tension of the water against air.[1] The surface tension is designated by σ and may be determined in a variety of ways, *i.e.*, by the force required to produce distorsion of the fluid surface, by the capillary rise of the fluid, or by measuring the maximum weight attained by a drop of the fluid falling from a tube.[2]

The work needed to increase the surface of the water drop is the product of the surface tension by the surface area (ω) *i.e.* surface energy $= \sigma.\omega$, or $\sigma = \frac{\text{surface energy}}{\omega}$ expressed in $\frac{\text{dynes}}{\text{cm.}^2}$. The effect of gravitation on larger droplets of water is to increase their area by flattening them into oblate spheroids.

Obviously if for air we substitute another surrounding medium, *i.e.*, oil, or if for water we substitute another droplet, *i.e.* mercury, the value of σ will change. Table VI gives a few values of σ.[3]

Opposed to surface tension is what Wo. Ostwald[4] terms "expansive surface energy" whose intensity is the so-called "internal pressure." This apparently depends upon the balance between the various forces acting on the molecules within the droplet, for it is increased by temperature and electrification. It is in effect the net internal energy of the droplet, and is one of the factors involved in solution. In fact solution is a condition of equilibrium reached between the internal forces of the solute and those of the solvent, and the mutual attraction between the solvent and solute. This equilibrium may be reached before true crystalloidal solution is effected; *i.e.*, tannic acid goes into crystalloidal dispersion in alcohol, but into colloidal dispersion in water.

TABLE 6.—VARIOUS VALUES OF SURFACE TENSION (σ)

	Dynes per square centimeter		
Mercury/air	436 0	Benzol/water	32.6
Water/air	75.0	Chloroform/water	27 7
Glycerin/air	65 0	Olive oil/water	22.9
Glue solution/air	48 3	Rosin/water	19.9
Olive oil/air	32 7	Oil of turpentine/water	12 4
Benzol/air	28 8	Ethyl ether/water	9 69
Chloroform/air	26 0	Isobutyl alcohol/water	1 76
Ethyl alcohol/air	22 0	Ethyl alcohol/olive oil	2 26
Ethyl ether/air	16 5	Olive oil/castile soap (1 to 4,000)	3.65

Returning now to our water drop on the oiled surface, Fig. 1, it may be seen there is a three-phase system involved—water/air/oil; and the following three interfacial tensions are involved: σ water/air, σ water/oil, and σ oil/air. Since: σ water/air > 75.

[1] Atmospheric constituents are also condensed on the surface

[2] J. L R. Morgan's drop-weight instrument, or Taube's staglamometer

[3] The figures are approximate only, as σ varies with the temperature

[4] See "Handbook of Colloid Chemistry," WO OSTWALD (trans. by M. H Fischer), Ch. 3.

σ water/oil + σ oil/air, the water droplet maintains its spherical shape. If, however, 22.9 32.7

a drop of oil be placed on water, it spreads itself out over the surface of the water, because: σ oil/air $<$ σ water/air $-$ σ water/oil. Thus the interplay of surface 32.7 75. 22.9

tension determines the distribution of fluids over interfaces, a fact of technical and especially biological importance. Glue or gum arabic dissolved in water, enable it to emulsify oil readily. In fact the lowering of the surface tension between phases is a forerunner of mixing or even solution; and as Willard Gibbs has demonstrated, substances which lower surface tension between two phases, tend to collect at their interface. This introduces a new idea—*adsorption*. *Adsorption* is essentially the concentration[1] of a dispersed substance at the interface between two phases. The power possessed by bone black to decolorize sugar solutions, of fullers earth to bleach oils, of platinum or palladium black to condense gases (*i.e.*, in automatic gas lighters), of charcoal to purify air (in gas masks during the recent war), are all examples of practical uses of adsorption; and a consideration of the adsorbents shows that they all have greatly extended surface.

The underlying cause of adsorption is found in the anomalous position of the surface atoms, previously referred to, they are attracted in three directions by atoms of like kind, whereas in the fourth direction they are in contact with the molecules of another substance, towards which they exhibit a residual surface attraction. Where one phase is solid and the other is fluid, the molecules of the fluid, and especially of substances dispersed in it, are condensed at the surface of the solid; and the most obvious examples of adsorption are found in this category. It is, however, an important factor in emulsions (fluid/fluid), resulting in the formation of emulsostatic surface films.

While adsorption has been commonly classed as a "physical" force, its dependence on chemical composition is marked, as is evident from the experiments of Bechhold,[2] who tested the adsorptive action of a series of chemically related compounds on acid and basic aniline dyes. The results were as follows:

TABLE 7

Substance	Acid dyes	Basic dyes
Naphthalin ($C_{10}H_8$) neutral	Faintly stained	Faintly stained
βNaphthol ($C_{10}H_7.OH$) acid	Faintly stained	Strongly stained
βNaphthylamin ($C_{10}H_7.NH_2$) basic	Strongly stained	Very faintly stained
Amidonaphthol ($C_{10}H_7OH.NH_2$) amphoteric	Stained	Strongly stained

Adsorption is frequently the precursor of chemical action. The adsorbed substance may diffuse into the adsorbent and there undergo irreversible changes, or it may by its mere concentration at the surface initiate chemical reactions. Catalyzers like platinum black and enzymes generally, are colloidal, and adsorption plays an important part in their activities. Frequently the adsorbed substance is coagulated at the interface, with the formation of a surface skin or pellicle. This is evident in solutions of dyes like fuchsin and methyl violet; it is responsible for the inactivation of enzymes by shaking, and the separation of albumin from aqueous solution in the foam produced by shaking with benzol or chloroform.

[1] In negative adsorption the reverse occurs, probably because the solvent is more strongly attracted than the solute.

[2] "Colloids in Biology and Medicine," p. 29. The work of Langmuir and others indicates that adsorption is the result of residual chemical forces.

Swelling is another common property of colloids, which is intimately connected with their enormous development of free surface, and with surface tension. Colloids are swollen only by substances which penetrate them; thus gelatin swells in water but not in benzol, whereas vulcanized rubber swells in benzol but not in water. The vapor of a solvent, being condensed by adsorption at the surface, acts like the liquid itself—gelatin swells in water vapor, and rubber in benzol vapor. The force with which fluids are absorbed by dry colloids is enormous. An old-fashioned method of splitting rocks is to drive in and then moisten baked wooden wedges. According to H. Rodewald starch exerts a swelling pressure of 2,523 atmospheres. The swelling is consequent upon the attraction of the solvent to the interfaces between the particles. The swelling of gelatine, fibrin, etc., is markedly influenced by electrolytes, especially by dilute acids and alkalis which strongly increase it. Apparently the hydrogen or hydroxyl ions are selectively adsorbed, and their electric charge tends to force the particles further apart. If the concentration is too great, however, the coagulative or "salting out" effect of electrolytes predominates, and shrinking occurs.[1] On the other hand, if gelatine is superdried at 130°C., it practically loses its swelling capacity, apparently because its particles are brought into such close proximity by the loss of their surrounding films of water, that they cannot be readily separated again.

Optical Properties of Colloids.[2]—The most striking optical characteristic of colloidal solutions is turbidity or cloudiness, which is due to the scattering of light by their small dispersed particles. If a powerful convergent beam of light be passed through a vessel containing water carefully redistilled through a silver worm, nothing is seen in the water on looking against a dark background at right angles to the beam. Upon mixing with the water a few drops of colloidal gold solution, the path of the light through the water at once becomes visible as a luminous cone. The same effect is seen on a large scale when a search light plays at night through a smoky or foggy atmosphere. This method was first used by Faraday (1857) and later by Tyndall, to demonstrate the optical inhomogeneity of colloidal solutions, and is known as the Faraday-Tyndall effect or Tyndall phenomenon. It might be considered a criterion of colloidal solution were it not for the fact that traces of colloidal impurities produce it, and it is to some extent shown by concentrated solutions of some crystalloid sugars (glucose, raffinose).[3]

The light scattered by colloidal particles is polarized, as may be seen by examining it with a Nicol prism or a selenite plate. Furthermore colloidal particles absorb, reflect, and transmit various fractions of white light, so that they frequently appear strongly colored. The color of colloidal gold solutions to transmitted light runs from yellowish and ruby red for the smaller particles, to purplish red, blue and violet or even brown, for the larger ones. In fact with colloids generally, as the size of the particles increases, the light absorption maxima shift towards the yellow end of the spectrum; or in other words the smaller particles show a brighter or more yellow shade. Rayleigh has shown that the blue color of the sky is due to the faint scattering of light by the molecules of the air, which is evident to us only when we look through a great depth of the atmosphere. Similarly distant mountains appear blue, especially on a hazy day when the atmosphere is full of colloidal particles of water, dust or smoke.[4] It is interesting to note that the apparent colors of many organized structures, are largely influenced by or entirely due to their colloidal nature (*i.e.*, feathers, mother of pearl, skins of fish.[5] Blue feathers usually owe their color, not to a blue pigment,

[1] Proctor and Wilson and J. Loeb believe that gelatin forms hydrolyzable salts and that its behavior is explainable on the basis of Downan's theory of membrane equilibrium.

[2] For fuller discussion, see E. F. Burton, "The Physical Properties of Colloidal Solutions," Chap. 5.

[3] Lobry de Bruyn and Wolff, *Rec. trav. chim des Pays Bas*, Vol. **23**, p. 155, 1904.

[4] Issuing steam becomes white when its particles aggregate to colloidal dimensions, and gradually become white again as it condenses to larger droplets.

[5] See "The Color of Colloids," by Wilder D. Bancroft; *Jour. Phys. Chem.*, 1919.

but to the reflection of the blue light waves with the concomitant absorption of the other waves. If the reflected blue light passes through a thin layer of yellow pigment, the feather looks green. Certain green tree toads turn blue when preserved in alcohol, which dissolves out the droplets of yellow oil from their skins.

Electric Properties of Colloids.—The particles of practically all colloidal solutions possess an electric charge, and under the influence of an electric current (difference of potential) move toward the electrode having the opposite charge. (Electrophoresis.) In general, when two substances are brought into contact, the one having the *higher* dielectric constant becomes *positively* charged, whereas the one with the *lower* dielectric constant becomes negatively charged (Coehn's Law). Since water has a high dielectric constant (80), most substances suspended in pure water become negatively charged and wander to the anode. On the other hand if suspended in oil of turpentine which has a low dielectric constant (2.23) they become positively charged and wander to the cathode.

If, however, electrolytes are present, Coehn's law is superseded by other controlling factors such as the adsorption of ions which may give their charge to the suspended particles. In fact Hardy found that in pure water albumen was amphoteric; in the presence of a trace of alkali it acquired a negative charge and migrated to the anode; but a trace of acid gave it a positive charge and it then migrated to the cathode. The following table shows the usual charge and migration tendency of a number of *aqueous* colloidal solutions.

TABLE 8

CHARGED + MIGRATE TO CATHODE (− POLE)	CHARGED − MIGRATE TO ANODE (+ POLE)
1. Hydrates of Fe, Cu, Cd, Al, Zr, Ce, Th.	1. Sulphides of As, Sb, Cu, Pb, Cd Halides of Ag.
2. Titanic Acid.	2. Stannic Acid, Silicic Acid.
3. Colloidal Bi, Pb, Fe and Cu (Bredig's Method).	3. Colloidal Pt, Au, Ag, and Hg, I, S, Se.
4. Albumen, Hemoglobin, Agar.	4. Gum arabic, soluble starch, gamboge, mastic oil emulsion.
5. *Basic Dyes.* Methyl Violet, Bismarck Brown, Methylene Blue, Hofman violet.	5. *Acid Dyes:* eosin, fuchsin, aniline blue, indigo, soluble Prussian blue.

Pectization and Peptization.—Briefly stated pectization means the coagulation of a colloidal gel and peptization its re-solution. If a small quantity of an electrolyte be added to a pure ruby-red colloidal gold solution, it changes to a blue or violet color, and deposits its gold as a fine blackish coagulum or precipitate.[1] By watching the coagulation of very dilute milk by acid in the ultramicroscope, the individual particles of the casein may be seen to gather gradually together into groups, whose motion becomes progressively less as their size increases, until they are no longer able to stay afloat, and finally coagulate in large grapelike clusters. Hardy believes that the particles of colloids adsorb the oppositely charged ions of the electrolyte; at the *isoelectric point* (that is when the charges on the particles become zero or are balanced) coagulation occurs.

[1] The amount in milligrams of protective colloid just sufficient to prevent the change to violet of 10 c c. of bright red colloidal gold solution, by the addition of 1 c.c. of a 10 per cent solution of NaCl, is called the "gold figure" or "gold number" of the protector.

If, however, an excess of electrolyte be added *all at once*, the isoelectric point may be passed before coagulation occurs, and the particles acquire a charge opposite to the one they had originally. Under such conditions, no coagulation may result.

Burton epitomizes the difference in action of various electrolytes as follows: "Two remarkable results are evident on comparing the coagulative powers of various electrolytes on colloids of different kinds; first, the coagulation depends entirely on the ion bearing a charge of sign opposite to that of the colloidal particle; and, second with solutions of salts, trivalent ions have, in general, immensely greater coagulative power than divalent ions, and the later, in turn, much greater than univalent. Acids and alkalis in particular cases act more strongly than the corresponding salts.

Very small quantities of electrolytes may actually stabilize colloidal solutions, their adsorption by the particles resulting in an electric charge that causes mutual repulsion. Frequently there are zones of stability representing concentration of electrolytes which cause no precipitation; but larger or smaller quantities produce coagulation. Thus a 1:32 mastic solution is flocculated by 0.10 and by 0.00025 molar aluminum sulphate, but not by a 0.0025 molar solution. Furthermore the coagulation may be reversible or irreversible, depending on the amount of the precipitating electrolyte. Thus albumen is irreversibly flocculated by 0.05 to 1.0 normal zinc sulphate; from $1N$ to $2N$ there is no flocculation; beyond $2N$ reversible precipitation begins, reaching a maximum at $4N$.

Oppositely charged colloids mutually coagulate each other. If more of one colloid is added than is necessary to satisfy the electric charge of the other, such excess acts as a protector, inhibits coagulation, and gives the mixture its charge. For this reason very minute quantities of protectors may act as sensitizers[1] or coagulants. Thus 0.0003 to 0.0001 pe rcent of gelatin flocculates mastic sols, and in the presence of one part of gelatin per million colloidal gold is flocculated by quantities of hydrochloric acid which otherwise would not affect it.

The coagulation of a colloid involves a liberation of energy, which may in some cases be determined calorimetrically. Thus Prange found that 1 g. of colloidal silver on precipitation by ammonium citrate developed 250.98 to 126.73 cal., according to the concentration of the silver solution. A still more profound coagulation of the resulting hydrogel by sulphuric acid, liberated an additional 60 cal. The liberated energy may appear in other forms than heat, *i.e.*, the so-called "vital forces," nervous impulses, and the mechanical energy of contracting muscle, are consequent upon changes in the degree of dispersion of the body colloids. The electrical energy released by the gymnotus and similar "electric" fish seems to be, and even self-luminosity may be, due to the same cause. In peizo-electrical effects and triboluminescence we have an analogous phenomenon, due to the aggregation of the constituent particles of crystals.

Peptization is the reverse of flocculation, a dispersion of groups into separate particles which once more acquire active colloidal motion which keeps them afloat and in solution. In fact the term peptization was coined by Graham to express the liquefaction of a gel, because of the strong analogy between digestion and colloidal disintegration.[2]

Colloidal Protection.—A most interesting and important fact regarding reversible colloids is that they can communicate their reversible property to irreversible colloids. The addition of gelatin (as little as 0.0001 per cent) to a solution of colloidal gold protects the latter against coagulation upon the addition of electrolytes, and permits it to redissolve after desiccation. Ultramicroscopic examination has shown that the gelatin does not affect the motility of the gold particles,

[1] Anaphylaxis is apparently a sensitization of this character.

See page 772. Chemical changes may accompany peptization.

thus disposing of the suggestion of Lobry de Bruyn that it acts by decreasing their motion. The idea advanced by Müller[1] that gelatin acts by increasing the viscosity and thus preventing the deposition of suspended particles, is disproved by the fact that quince-kernel gum, notwithstanding its viscosity, exercises no protective action,[2] whereas the small quantities of gelatin necessary to produce this effect cannot appreciably increase the viscosity, and actually permit gold particles to settle if they are large enough to do so.

The action of reversible colloids in opposing group-formation, is of great technical importance, for in many cases it permits them to hinder, modify and even prevent coagulation, precipitation and crystallization. Thus, in the absence of the colloid a dilute solution of nitrate of lead deposits beautiful glistening crystals of metallic lead upon a strip of zinc immersed in it, whereas in the presence of some glue the deposit appears dull and amorphous.

Dialysis.—Colloid solutions possess a small but definite diffusibility through colloidal septa (parchment paper, bladder) as was recognized by Graham (see p. 772). Graham's original form of dialyzer may be made from a wide-mouthed bottle whose bottom has been removed.[3] The mouth is closed by a piece of bladder or parchment paper tightly bound on, the solution to be dialyzed is poured in, and the bottle immersed about half way in water contained in a larger

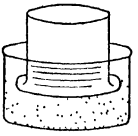


FIG. 2.—Dialyzer.

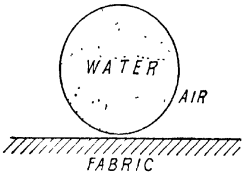


FIG. 3.

vessel (see Fig. 2). Most of the crystalloids diffuse through the membrane into the outer water, which should be frequently renewed; while most of the colloid remains in the interior bottle, and may be thus obtained in a purified condition. Improved modern dialyzers consist of parchment or collodion sacs, discs or thimbles, or even of whole bladders, which have the advantage of a larger dialyzing surface.

SOME PRACTICAL APPLICATIONS

Shower-proofing of Fabrics.—Ordinary textile fabrics are readily wet by rain; but if coated with a surface film of wax or the like (aluminum stearate), the falling droplets roll off—"like water off a duck's back." This waterproofing effect is readily understood if we consider the interfacial surface tensions involved (see Fig. 3). These are:

1. Surface tension water/air, denoted by σWA
2. Surface tension water/fabric, denoted by σWF.
3. Surface tension air/fabric, denoted by σAF.

Practically speaking, the surface attraction of the untreated fabric for water

[1] *Ber.*, 1904, Vol. **37**, p. 11.

[2] According to Zsigmondy, quince-kernel gum acts as a protector with mose substances.

[3] A lamp chimney will answer very well.

is so great (*i.e.*, σWF is so small[1]), that both the surface film or skin of the rain-drop and the air film on the fabric, are burst; the rain-drop spreads itself out on the fabric and is absorbed into its pores. That is wetting occurs if

$$\sigma\text{WF} < \sigma\text{WA} + \sigma\text{AF},$$

or

$$\sigma\text{WA} > \sigma\text{WF} - \sigma\text{AF}$$

In the case of the treated fabric, σWF is very much *increased;* becoming in fact the surface tension water/wax, for surface tension is only skin deep. Therefore,

$$\sigma\text{WF} > \sigma\text{WA} + \sigma\text{AF}$$

or

$$\sigma\text{WA} < \sigma\text{WF} - \sigma\text{AF}$$

and no wetting takes place.

Flotation.—The understanding of what happens in flotation will be much simplified, if we bear in mind that, notwithstanding the presence of many disturbing and variable factors, there are two main triphasic systems involved. These are:

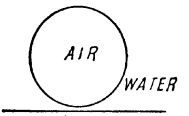


FIG. 4.



FIG. 5.

1. Ore/water/oil from which the true ore (usually a sulphide) must emerge with a film of oil which enables it to be taken up by the air bubbles and thus floated with the froth, while the gangue is wetted and flowed off at a lower level.

2. Air/water/oil which yields the bubbles to float the oiled sulphide. Referring to the diagram (Fig. 4), and denoting

1. Surface tension water/oil by σWO
2. Surface tension oil/sulphide by σOS
3. Surface tension water sulphide by σWS

then the oil will distribute itself over the interface water/sulphide (*i.e.*, the sulphide will be oiled)

if

$$\sigma\text{OS} < \sigma\text{WO} + \sigma\text{WS}$$

or

$$\sigma\text{WO} > \sigma\text{OS} - \sigma\text{WS}$$

The second system is illustrated by diagram (Fig. 5). Denote

1. Surface tension water/air by σWA
2. Surface tension water/oil by σWO
3. Surface tension air/oil by σAO

The oil or some of its constituents distribute themselves at the interface water/air because

$$\sigma\text{WA} > \sigma\text{WO} + \sigma\text{AO}$$

75 23 33 (approximate values)

[1] It should be borne in mind that the surface tension *decreases*, as the attraction between the phases *increases*. In fact when the positive surface tension in a two phase system becomes zero, solution may take place

This yields air bubbles with a more or less stable surface film, *i.e.*, a foam or froth. This film is miscible with the oil film on the sulphide, although not necessarily identical with it, because there may be a separation of the constituents of the oil by differential absorption. The oiled sulphide particles therefore act like oil, and, distributing themselves at the interface water/air, are attached to the air-bubbles and lifted or floated to the upper froth layer, if they are not too heavy or are not knocked off. The gangue is not oiled, and flows off at a lower level.

In the foregoing no account has been taken of complicating factors which are always present; and while space will not permit an exhaustive discussion of them and their results, the most important will be considered.[1]

1. *Water.*—Here are found dissolved air, crystalloids and colloids. The dissolved air aids in bubble-formation by reducing the internal pressure of the water. For the most part the crystalloids, especially *acid* electrolytes, act beneficially, being adsorbed by coagulating the fine slimes, clay, etc., which then tend to repel the flotation oil, recalling the old-fashioned household expedient of moistening the mouth and throat with orange or lemon juice before taking castor oil, and thus avoiding the taste. Some electrolytes, especially alkalis (*i.e.*, Na_2CO_3) in small percentages are powerful deflocculators, and by reducing the surface tension water/oil and water/sulphide tend to emulsify the oil, wet the sulphide, and deflocculate the slimes. Humic substances especially when converted into alkali salts, and protective colloids generally, act in like manner—the injurious effects of glue are well known. Colloidal clay or very fine gangue act similarly—"fat" clays will emulsify oils, coal tar and asphalt.

2. *Ore.*—Outside of soluble impurities which dissolve in the water, the fineness of grinding is most important. The gangue should be fine enough to flow off, but not so fine as to cause the undesirable effects just referred to above. If the sulphide particles are too large, the air bubbles cannot lift them, or they are easily knocked off; if they are too small, there is a great loss in efficiency, for the surface of the bubbles may be satisfied by a layer of small particles which represents a small weight of sulphide. The subjoined diagram (Fig. 6), makes this obvious.[2] The results may also be adversely affected by the surface oxidation of the sulphide.

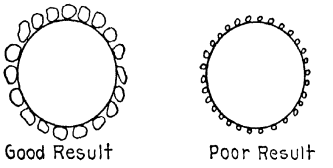


FIG. 6.

3. *Oil.*—This is deserving of the most intensive study, since it is the factor most readily controlled; and besides the great and sudden development of the art of flotation has turned the various oil markets topsy-turvy, necessitating a constant search for new oils or combinations not only from financial considerations, but also because of actual shortage in the supply. Since conditions are different at each plant, and since different lots of ore even from the same mine may vary, a careful study is necessary to determine what oil or mixture is best, and also to know how to meet changing conditions. Particularly useful will be a determination of the foam-producing factor as opposed to the sulphide-oiling factor. Some so-called soluble oils give even better results than coal and wood tar distillates. According to recent patents, a wide variety of substances may replace oils.

Some idea of the importance of flotation in the mining industry may be formed from the subjoined table published by the U. S. Bureau of Mines.

[1] Mechanical agitation and temperature exercise considerable influence. Callow estimates that with four different oils, three oil percentages, two pulp densities, and two temperature changes, there are about 60,000 possible different combinations of conditions

[2] The layer of tiny adhering ore particles form an armadillo-like armor about the air bubbles, which to a large extent protects them from coalescence and destruction.

MONTHLY CONSUMPTION OF FLOTATION OILS IN UNITED STATES

Type of ore	Monthly tonange of ore		Monthly consumption of flotation oils, beginning of 1916, pounds				
			Wood products				
	Beginning 1916 (tons)	End of 1916, estimated (tons)	Pine oil	Pine tar oil	Eucalyptus	Creosote	Turpentine
Copper.....	1,248,000	1,942,000	59,300	750		417,000	1,500
Zinc and complex .	248,000	350,000	60,750	667		262,500	3,330
Lead	115,000	136,000	3,900		216	121,000	
Gold and silver	45,700	123,000	9,830	750		40,250	
	1,656,700	2,551,000	133,780	2,167	216	840,750	4,830

MONTHLY CONSUMPTION OF FLOTATION OILS, BEGINNING OF 1916, POUNDS

Type of ore	Oleic acid	Coal products			Petroleum	
		Tar	Creosote	Cresol	Crude	Fractions
Copper	...	677,000	403,000	8,340	79,000	1,702,000
Zinc and complex	5,830	10,670	46,500		157,000	41,000
Lead	...		9,250			660
Gold and silver .	.	27,450	4,920		7,090	6,250
	5,830	715,120	463,670	8,340	243,090	1,749,910

Lubrication.—The consumption of petroleum is increasing so rapidly that a material decrease in the supply, if not actual exhaustion, lurks in the not far distant future. W. B. Hardy in a trenchant paper (*Journ.* Soc. Chem. Ind., Vol. **38,** No. 2, p. 7t, 1919), has shown that we may with confidence look to colloid chemistry to aid us in finding the lubricants of the future.

Glass surfaces selectively adsorb from the air rather more of the atmospheric impurities than of the elementary gases and water vapor, yielding a film about $1\mu\mu$ (1×10^{-7}cm.) thick, which Lord Rayleigh termed "grease" because it has the general properties of an oil.[1] For this reason a new or raw glass surface has different mechanical properties than a satisfied or neutral surface.

"It is not possible to get a raw surface of glass.[2] One cannot cleave glass; but the 'grease' film may be removed by rubbing the surface under water. Soaking is insufficient; actual vigorous rubbing is necessary, preferably with the finger tips

[1] This adsorbed layer of "grease" tends to make pipettes and burettes deliver inaccurately, so analysts remove it by oxidation with bichromate.

[2] Raw surfaces are readily made by cleaving mica, and if immediately put together again, they adhere so strongly that they withstand a powerful lateral pull, and usually tear the surface when finally separated.

until a peculiar clinging feeling is produced; the same which is felt when the edge of a finger bowl is rubbed so as to give out a musical note. A surface cleaned in this way has some remarkable mechanical properties, the most striking being that two cleaned surfaces seize when pressed together with a relatively small force. This may be demonstrated very simply by measuring the tangential force needed to produce slipping. That true seizing occurs is proved by the tearing of the surfaces, which takes place in the act of slipping.

"The function of lubricants is to keep the applied surfaces in the neutral condition by maintaining a 'grease' film on each. Not all fluids, however, can act in this sense as lubricants for any particular surface such as that of glass. Water, ether, alcohol, benzene, and strong ammonia are apparently entirely incapable of maintaining a lubricating film on glass. Seizing occurs just as readily when they are present as it does with cleaned surfaces. Glycerin differs from the fluids mentioned above in the fact that though it will not maintain a lubricating film it does prevent seizing when present in excess. For instance, the maximal tangential force which a pair of cleaned surfaces would support without slipping was measured in grams, 55. Flooding the surfaces with water, benzene, alcohol, etc., left this value unchanged. When a film of glycerin was deposited on the surfaces the force still stood at 55, but it fell to nine when the surfaces were fully flooded with glycerin.

"The expression 'film' used above denotes a layer of fluid on the solid surface of the order 10^{-7} cm. in thickness. With a true lubricant the facility for slipping is maximal when a layer of this excesive tenuity separates the solid faces and nothing is gained by increasing the thickness of the layer.

"Thus with castor oil the weight required just to start one face of glass slipping over another was 10 g. when only the invisible film of fluid mentioned above was present, and it was still 10 g. when the surfaces were flooded with oil.

"Some fluids indeed seem to lubricate better in thin than in thick layers, to act that is to say in the contrary way to glycerin. Acids as a class behave in this way, the solid faces again being of glass.

PULL IN GRAMS

	Film	Flooded
Acetic acid	40	47
Sulphuric acid	37	47
Oleic acid	10	13

"If these results can be fully substantiated it will be an important and striking physical fact likely to throw much light upon the process of lubrication. One broad conclusion emerges from these facts, namely, that lubrication depends wholly upon the chemical constitution of a fluid, and the fact that the true lubricant is able to render slipping easy when a film of only about one molecule deep is present on the solid faces, suggests that the true lubricant is always a fluid which is adsorbed by the solid face. If this be so then the problem of lubrication is merely a special problem of colloid physics."

Some solids, notably graphite, are lubricants themselves. But the chief function of graphite seems to be as an aid to lubrication by oil. The graphite is disintegrated in the bearing and besides filling up relatively large imperfections, its colloidal particles are adsorbed by the iron, forming in reality a graphite surface which has a lower surface tension against oil than iron has. Practically this means that the oil film adheres more strongly to the graphitized surface and therefore needs greater force or pressure

to break it down; *i.e.*, the bearing will stand greater speed and pressure. Acheson's "oildag" consists of a paste of colloidal graphite dispersed in oil; a small percentage is mixed with the lubricating oil and feeds with it through the finest orifices. "Aquadag" is the corresponding water-soluble product, stabilized with tannin.

Colloidal Fuel.—What promises to be one of the most far-reaching advances made under the stress of the recent war, when necessity literally was the mother of invention, is the discovery that by means of a suitable fixateur or peptizing agent and suitable treatment, very large percentages of cheap tars and finely powdered coal waste may be held dispersed in fuel oil with a sufficient degree of permanence to enable the mixture to be stored, piped, atomized and burned practically like fuel oil itself. Since it will at one stroke relieve the drain on the earth's rapidly diminishing stores of petroleum, as well as lead to the efficient utilization of all kinds of coal waste (culm, screenings, dust), inferior fuels (peat, lignite), and even cellulose waste (slabs, saw-dust), this new composite fuel may be hailed as a powerful factor in the conservation of our natural resources, and a lasting benefit to mankind.

Realizing the vital importance of the oil supply to the Allies in the conduct of naval, military and manufacturing operations, the German submarines bent every effort to destroy tankers, and Marshal Foch is said to have cabled America: "If you don't keep up your petroleum service, we shall lose the war." While the Allied navies were dealing with this peril in a most decisive fashion, Lindon W. Bates, head of the Engineering Committee of the Submarine Defence Association, with the assistance in laboratory matters of Dr. S. E. Sheppard and other chemists of the Eastman Kodak Laboratory, courteously opened to him, developed "colloidal" fuel, which by practically doubling the usefulness of every oil cargo, would of itself have materially assisted the defeat of the enemy efforts.

Coal or other combustible solid is prepared for dispersion by being pulverized so that about 95 per cent passes through a 100 mesh, and 85 per cent through a 200-mesh screen. This, of course, means that by far the greatest weight is in particles hundreds and thousands of times larger than colloidal dimensions. But we should remember that violent motion of the colloidal particles causes the Brownian movement of much larger particles, as is the case in milk (see p. 765) where the fat globules can be seen oscillating about under the ceaseless bombardment of the casein ultramicrons. It has been found that a fluid fuel may be made containing as much as 40 per cent by weight of powdered coal, and mobile pastes with up to about 75 per cent; and mobile gels may be produced both from the liquid and the pastes.

The exact nature of the fixateur, peptizing agent, and treatment is withheld pending the issuance of patents here and abroad, but it is stated that ordinarily between 0.5 per cent and 1.5 per cent of the essential component of the fixateur is used, whereas about 0.1 per cent exercises a noticeable influence. The amount of protecting agent is determined by the nature of the mixture desired, the components, and the degree of permanence desired. The bulk of the particles does not begin to settle until the period of "life" has passed. This period is subject to control within reasonable limits and may be days or months in duration and may be relative or nearly absolute in degree. Settling thereafter begins gradually but proceeds progressively unless a gel has formed. Heat and agitation revivify the fluid fuel, and the paste may be kept for years. The period of adequate stability may be regulated to meet requirements, days for power plants, weeks and months for ocean going vessels and for central storage stations.

Being heavier than oil or even water, colloidal fuel compresses in a unit volume the maximum thermal value, thus economizing storage space; and it may be stored

under and extinguished by water, thus avoiding fire risk. Its operative efficiency is high, for when sprayed into the hot firebox, the oil-permeated particles of carbonaceous matter are still further atomized by the sudden gasification of their imbibed oil. It possesses the advantages of fuel oil over coal, absence of smoke, dust and ash, practical elimination of labor in loading into storage space and in firing, with resultant saving in time for "coaling" and for raising steam. As in the case of oil, a protective smoke screen may readily be produced by over-firing, and the fire is subject to instant control.

Smokes.—While it is an ancient principle of strategy to attack an enemy under cover of natural fog or mist, the recent war led to an enormous development of artificial smokes as aids to naval and military offensive and defensive operations. Like the cuttlefish, steamers strove to escape pursuing submarines in colloidal clouds of their own making, and our soldiers frequently crept to the attack under a protective smoke barrage. Ammonium chloride, stannic acid, sulphur trixoide, phosphorus, coal, and oil smokes were among the cloud-forming substances used, and some of the interesting work of the Dispersoid Section, Research Division, Chemical Warfare Service, U. S. A., has been published.

Tolman and Vliet[1] describe an easily constructed Tyndallometer for determining the strength of the Tyndall beam in suspensions, colloidal solutions, smokes, and mists, and find it proportional to the concentration, unless too high a concentration allows opacity to affect the results. In general for smokes, increased subdivision results in increased Tyndallometer readings. Gaseous dispersoids have a relatively short life, for the coagulation and precipitation of the smoke particles begins immediately, and is favored by concentration (meaning closer proximity of the particles) and by fineness of subdivision (meaning greater speed of and more collisions between the particles). It is therefore impossible to raise the optical density of a smoke beyond a certain point, by the introduction of further smoke material.

Wells and Gerke[2] describe an oscillation method for determining the size of ultramicroscopic particles, by measuring photographically their oscillation amplitudes in an electric field which is rapidly reversed by a rotating commutator. The formula used, based on Stokes' Law, is

$$Xe = 3\pi\eta dv$$

where X = electric field in volts per centimeter
e = electric charge (assumed to be 1 electron) = 1.59×10^{-20} e.m.f.
η = viscosity of the dispersion medium (air).
d = diameter of the particle in centimeters
v = velocity of the particle (= oscillation amplitude × frequency of field reversal)

which gives

$$d = 9.3 \times 10^{-10} X / v$$

Particles in one specimen of tobacco smoke were estimated according to this method to be about 2.75μ; in another specimen, from 0.8 to 1.0μ.[3]

As an instance of the commercial utilization of smoke, may be mentioned the practise of burning smudge pots in orchards especially in spring or early summer, when weather condition indicate that the tender blossoms or fruit are apt to be damaged by frost. The heat emitted by the pots is a factor, but the efficacy is partly due to the dense clouds of smoke given off by the burning smudge oil. This remedy is

[1] *Jour. Am Chem Soc.*, Vol. **41**, p. 297 *et seq.*
[2] *Jour. Am Chem. Soc.*, Vol **41**, p. 312 *et seq.*
[3] See also Zsigmondy's observations on tobacco smoke. "Colloids and the Ultramicroscope," p. 196.

of course useless in very cold weather, and serves to prevent only what agriculturists call a light frost, which has for its precursors a still clear atmosphere and a temperature approximating the freezing point. No such frost occurs on cloudy or windy nights.

In the absence of smoke, moisture deposits upon leaves, fruit and other surfaces furnishing nuclei, and congeals into ice crystals or "frost" when the slight heat thus generated by condensation, is dissipated into the surrounding cold atmosphere, the freezing being also facilitated by the evaporation of part of the deposited water. The smoke, however, furnishes throughout the entire lower atmosphere, innumerable nuclei for the deposition of moisture and the widely distributed and relatively larger amount of heat thus set free is sufficient to help carry the temperature above the freezing point. The smoke fog furthermore forms a kind of protective blanket, which reflects the terrestrial heat and prevents its dissipation.

On the other hand fine sulphuric acid mist, cement and smelter fume and the like, are types of injurious industrial smokes which are now electrically coagulated by the well-known Cottrell process. Although this process was originally worked out to abate the dust and fume nuisance, cement and blast-furnace dust are now yielding considerable potash, while in smelter fumes are found large quantities of arsenic, selenium, tellurium and other substances. The use of the high tension discharge to dispel fog and thus prevent collision at sea, is a possibility previously suggested by Sir Oliver Lodge.

Ultracentrifugation.—The non-homogeneity of ordinary crystalloid solutions was demonstrated by van Calcar and Lobry de Bruyn, who caused about three-eighths of the sodium sulphate in a saturated solution to crystallize at the periphery of a rapidly rotating centrifuge. To do this required several hours at about 3,000 r.p.m. If such results can be accomplished with crystalloid molecules, it is to be expected that larger colloidal groups can be separated from solution by centrifugal force, the main factors being the viscosity of the dispersion medium, diameter of the centrifuge, speed of rotation, and length of time the centrifugal force acts.

Certain commercial sized centrifuges rotate between 15,000 and 20,000 r.p.m., and develop a separating force over 15,000 times as great as gravity. Such machines naturally have a much wider range of usefulness than their prototype, the turbine-driven cream separator, which years ago marked such a big improvement in both speed and efficiency, over the old-fashioned "pan" or gravitation method of separating emulsified butter fat from milk. Thus for example, with modern ultracentrifuges, varnishes, nitrocellulose lacquers, vegetable oils, gelatin liquors may be clarified; blood corpuscles may be separated from the serum in making blood albumen and sera; and there may be recovered from waste wool scouring liquor, wool grease of light color, suitable for refining into lanolin, instead of the dark degras yielded by the cumbersome acid coagulation method. The use of the laboratory ultracentrifuge capable of making 40,000 r.p.m. opens a wide field for analytical and physiological research, for with it can be avoided a factor that often causes trouble in filtration or ultrafiltration, namely adsorption by the filter medium.

Miscellaneous Practical Applications.—The use of protective colloids in electrodeposition is well known, use being made of them on a large scale in the Betts' process for electrolytic lead. Colloids such as glue, dextrin, tannin, are used to prevent the formation of hard scale in boilers. The successful treatment of sewage largely depends on the successful precipitation of colloids, as does also water filtration.

Many other practical applications are mentioned in the reference given below. These include rubber, brewing, chemical analysis, colored glass, metallurgy, gems, medicine, biology, paper, dyeing, nitrocellulose, petroleum, asphalt, mineralogy, geology, tanning, etc. Most journal articles of value are abstracted in "Chemical Abstracts" or "Kolloid Zeitschrift."

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SECTION XXIV

METALLURGY OF ZINC

By Walter Renton Ingalls[1]

The art of zinc smelting is simple in principle, but complicated in practice. It depends upon the reducibility of zinc oxide by carbon, or carbon monoxide, or both. Consequently zinc sulphide—blende—must first be roasted to obtain the oxide. Zinc silicate ($ZnO.SiO_2$) is reducibledirectly by carbon.

Zinc oxide begins to be reduced by carbon at 1,125°C., but at that temperature zinc is reoxidized by carbon dioxide if the latter be present in more than 0.2 per cent. With increase of temperature the permissible percentage of carbon dioxide increases also, until at 1,500°C. there may be 0.76 per cent.[2] This fact is of supreme importance in the metallurgy of zinc. It explains why metallic zinc may not be distilled in a blast furnace and why the product is blue powder in one-stage smelting in the electric furnace. Zinc oxide can be reduced in the blast furnace just as it is in the Wetherill furnace, which is a species of blast furnace, but in the Wetherill the reduced zinc is then intentionally burned to oxide. By limiting the presence of carbon dioxide, combustion of the zinc may be avoided, but the oxidation that results in blue powder cannot be avoided. This is why the reduction-distillation of zinc is limited to relatively small retorts, in which the necessary and peculiar conditions can be maintained, and why the process must be so arranged as to be divisible into stages. Even so, although it is possible to establish the condition of very low carbon dioxide in the gas issuing from the retort during the period of active distillation, it is seldom possible to attain the minimum theoretically required and consequently there is always some production of blue powder.

As practically conducted, zinc distillation is an intermittent process, divided into four stages, *viz:* (1) The maneuver, during which the spent residues from the previous charge are withdrawn, broken retorts are replaced, all retorts are recharged, etc. This requires 3 to 5 hr. (2) Preliminary reduction, during which water is expelled, hydrocarbons are driven off, and the oxides of metals other than zinc, such as iron and lead, are reduced. During this stage the temperature of the retorts is raised gradually. The issuing gas is first pure coal gas and burns with a luminous flame at the noses of the condensers. This flame becomes less bright as the reduction of the metallic oxides begins and the percentage of carbon monoxide increases, gradually becoming purple. When the flame becomes tinged with bluish-green the beginning of zinc distillation is indicated. This marks the end of the second stage of the process, although the dividing line is not sharply drawn. When zinc begins to distil and condense the percentage of carbon dioxide in the gas is still high and consequently there is much formation of blue powder at this time. (3) Active distillation, during which the zinc is reduced and distilled rapidly. (4) Waning distillation, during which the last

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[2] Bodländer, *Zeit. für Elektrochemie*, VIII, xliv, 833–842

part of the zinc is expelled, the average rate of hourly condensation during this period being only about one-half that of the previous period. A high temperature is maintained and the resistance of the retorts, relieved of the endothermic reaction within them, is tested most severely. Finally, all of the zinc is expelled that can be at the temperature used, the condenser flames become purple again, the cycle has been completed and preparations are made for the maneuver of the next day.

From the foregoing will be seen one condition that stands in the way of making zinc reduction-distillation a continuous process, *viz.*, the necessity for performing the second stage separate from the third. In practice this is done as one of the steps in a 24-hr. cycle in the distilling furnace, but it may be done in a separate furnace as a separate act and then zinc distillation may be conducted continuously. This has been proved by electric furnaces operated on preheated, or prereduced, charges. The same idea of prereduced charges is actually, though not generally, used in practical pyrometallurgy, not to the extent of enabling continuous distillation, but enough to relieve the retorts of some of their work and extend the time available for active zinc distillation.

However, there is another important condition that stands in the way of continuous distillation, though it is not insuperable, *viz:* Intimate contact of zinc ore and carbon is necessary, which implies fineness of grains. Indeed, zinc ore being so largely the product of concentrating mills, including the excessively fine flotation slimes, it comes to the distiller fine anyhow. Now, when a retort is charged with fine ore a rod must be run through the top (this is called "spiessing") in order to afford a channel for egress of the gas and vapor during the early stage of distillation. However, the gas and vapor must seep up through the charge itself in order to get into the channel. Under certain conditions, *e.g.*, too great depth, excessive fineness, etc., it may be unable to do that easily. The result then may be the accumulation of such internal pressure that the entire charge will be blown out of the retort. This is why the distillation of ore ordinarily fine is practically limited to the depth that it has in the Rhenish retort, *i.e.*, about 12 in. For the distillation of coarser charges in Upper Silesia deeper muffles were formerly used, but when they began to treat richer and finer ores the Silesian distillers had to adopt the Rhenish retort.

The same condition applies to vertical retorts designed for continuous operation, although the earlier designers did not think of it. The gas and vapor could not get out. One or more inventors thought subsequently to meet this condition by arranging a row of outlets down the shaft. It is possible, also, that the condition may be met in other ways. However, with the exception of the Roitzheim-Remy furnace that was introduced in Germany just before the war, about which no thoroughly satisfactory information was communicated, and since then none at all, continuous distillation has not become established in zinc pyrometallurgy.

It will help in the consideration of the whole subject of zinc pyrometallurgy to fix these fundamental principles of practice well in the mind. There is another one, namely, the matter of temperature of distillation, on which depends largely the extraction of the zinc, the quality of the primary product and the cost of the process.

Although zinc oxide begins to reduce, under certain conditions, at 1,125°C. the speed of the reaction is greatly increased by increase of temperature, and since it is for technical considerations important in practice to complete the working of a charge in 24 hr., it is essential in practical smelting to conduct the operation at a considerably higher temperature. Given a certain time for the distillation, which is commonly about 18 hr., the remaining 6 hrs. being occupied in

discharging and recharging the retorts, the higher the temperature, the more complete will be the extraction of the zinc. But here enter other complications. The singulosilicates of iron, lime, etc., begin to form at about 1,200°C., and as the temperature rises further more infusible slags can form, and the gangue of the ore containing these elements may give rise to slags which quickly corrode and destroy the retorts in which the distillation of the zinc is being conducted, to such an extent indeed as to make the process impracticable. Moreover, with increase of temperature other metals, especially lead, distil over with the zinc, necessitating a further refining of the latter in order to produce a marketable quality of metal. An ordinary temperature of distillation is 1,250 to 1,350°C. The performance of the process at 1,200°C. is known as "slow driving," while 1,400 to 1,450°C. is "hard driving."

American smelters lean to "slow driving" while Europeans adhere to hard driving. In either way there is some variation in the management of the furnace. Having arrived at the third stage of the process one smelter may raise the temperature quickly and maintain a high temperature right through the third and fourth stages while another may raise it more gradually and attain a maximum during the fourth stage when he is "pinching" the charge. As already pointed out, with increase of temperature other metals, especially lead, distil over with the zinc. Given the lead contents of charge and spelter, an experienced metallurgist can tell pretty nearly what was the temperature of distillation. American smelters make a practice of keeping separate their first draw of metal, which will be higher in cadmium and lower in lead than the second draw. The third draw will be highest in lead. European smelters, distilling uniformly at high temperature, are apt to make a leady spelter, which has to be refined by melting in a reverberatory furnace and allowing the excess of lead to separate by gravity. This has the incidental advantage of equalizing the spelter and producing slabs of uniform composition. Spelter molded directly from the drawing kettles is apt to be irregular and there is more or less complaint against American brands on this account.

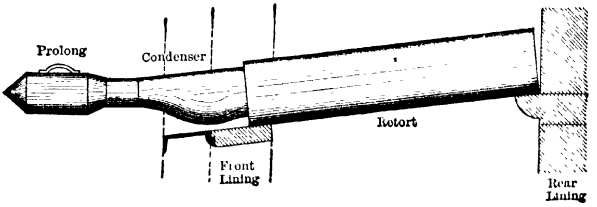


FIG. 1.—Retort, condenser and prolong

The matter of temperature introduces consideration of the behavior of the gangue of the ore, for the higher the temperature the more dangerous become the slags. The historic method of taking care of the slag is to have present a great excess of reduction material to absorb and hold it like a sponge, but in modern practice care is taken not to permit the formation of anything like an easily fusible singulo-silicate, but so to compound the charge that the slag will be a bisilicate or trisilicate. The retorts must be as strong, dense, and non-corrodible as it is possible to make them, and the lining of the furnace, in fact the general structure, and especially the middle wall, or middle ledges, must be of the maxi-

mum durability. The successful withstanding of a temperature of 1,550°C. for a campaign of upward of 3 years requires refractory material, mason's work, and general furnace design of a high order of excellence.

Complying with these conditions, good practice tends strongly to hard driving, for the extraction of zinc is greatly increased without corresponding increase in the consumption of coal as compared with slow driving. The European smelters have been hard drivers because their coal has been dear, even in pre-war times. Note must here be made that a furnace designed for the distillation of a certain ore at a relatively low temperature cannot necessarily be speeded up by simply raising the temperature. In so doing the capacity of the condensers might be overtaxed and zinc distilled too rapidly might be forced to burn uncondensed at their noses. Reference may here be made to the subject of prolongs, sheet iron extensions of the condensers. European distillers use them generally; American but rarely. They save considerable zinc escaping from the condensers, but in American practice this is deemed insufficient to compensate for the extra labor of taking them down and putting them up at each draw. With the Rhenish and Silesian furnaces drawing is less frequent, nor do the prolongs have necessarily to be taken down during drawing.

This statement of general principles outlines the complexity of the art of zinc distilling in arriving at the most economical balance among many conflicting conditions. Within the present limits of space it is impossible even to hint at many details of the art. The manufacture of retorts and condensers, the design of distilling furnaces, the organization of labor for their operation, the matter of density of charge, these and many other things are subjects for voluminous analysis and discussion. Bulky treatises are devoted to them without exhausting the subjects. The reader is referred to Ingalls on "Metallurgy of Zinc and Cadmium," Lodin on "Metallurgie du Zinc," Liebig on "Zink und Cadmium," Hofman on "Metallurgy of Zinc and Cadmium," and Prost on "Cours de Metallurgie des Metaux autres que le Fer."

Coming to practical application, the first step is to roast the ore, blende now being the common ore. Out of many furnaces that have been designed and used, but few need here be mentioned. Where labor conditions permit hand-roasting, as in Europe they have done heretofore, the Delplace kiln is the favorite. This is a superior form of shelf-burner, so designed as to be very economical of fuel. American smelters use commonly the Hegeler furnace, which is clumsy and costly. European smelters and one American have been successful with the Spirlet, which is distinctly a mechanical furnace. Other mechanical furnaces, such as the Merton and the Ridge, have been tried here and there but have not established themselves generally. The metallurgy of zinc still lacks a thoroughly good mechanical muffle-furnace.

Furnace Design.—Respecting distilling furnaces the designs that are in successful use are of great variety. It is even difficult to classify them. My present effort to do so will be different from anything attempted heretofore.

In the first place I shall distinguish between the method of heating and the metallurgical type, which is roughly equivalent to distinguishing between the inferior structure and the superior. Confining our attention for the moment to regenerative furnaces, and the modern furnace is almost necessarily confined to this class, we may have either the counter-current regenerative or the reversing regenerative. The latter may have regeneration for both gas and air or for air alone. The checker-works may be arranged longitudinally, or transversely. In the laboratory, or combustion chamber, of the furnace the flames may rise vertically, leap over the middle wall, and descend on the other side, or they may reverse from end to end of the

surface traveling longitudinally and horizontally. They may issue from ports in the middle wall. This is mainly a problem of efficient combustion and equable heating. The desiderata are a temperature around the retorts as nearly even as possible and a combustion product escaping to the chimney at only 200 to 300°C. as it leaves the furnace. There are designs, such as the Welzer (Overpelt) and Neureuther-Siemens, that permit a ton of ore to be distilled with as little as 0.9 ton of coal. The best of the counter-current furnaces and the Hegeler furnace, so extensively used in the United States, in which the heat recuperation is effected through the medium of a waste-heat boiler cannot equal that figure.

Metallurgically, distilling furnaces may be classified as Belgian, Silesian and Rhenish. The distinguishing features are comprised within the superior structure, which may be combined with different forms of the inferior. Thus, a Rhenish top

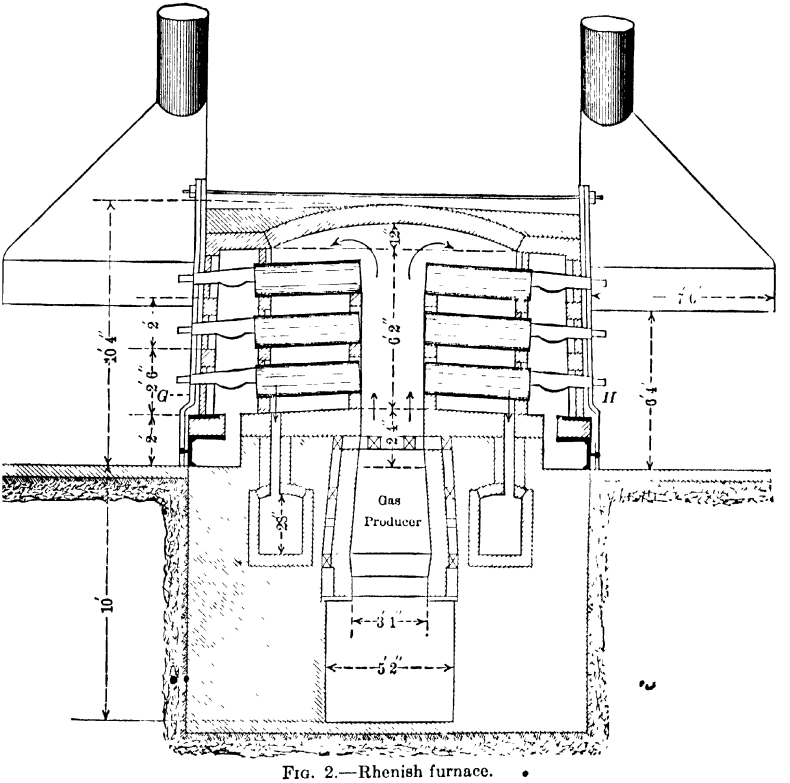


FIG. 2.—Rhenish furnace.

may be put upon a counter-current regenerative base or upon a reversing regenerative base, or indeed the base may be simply designed for direct-firing. The real difficulty is encountered in drawing a sharp definition among the three metallurgical types and especially between the Rhenish and the other two. This difficulty is not unnatural, considering the history of the types. Originally there were only two types of distilling furnaces, *viz.*, the Silesian and the Belgian, which were quite distinct. Later there

was developed a compromise, known first as the Belgo-Silesian and later as the Rhenish. Being a compromise, in which features were adopted from both the prototypes, the characteristic features of each were not everywhere borrowed to the same degree, and consequently there has always been some uncertainty as to just what constitutes the pure Rhenish type. I will offer the following generalization.

The Rhenish distilling furnace is one possessing a combustion chamber in which are suspended three double rows of retorts so that the flames can circulate around all of them. The furnace has two facades, or fronts, and is roofed by a single arch springing from the top of one front to the other. The support of the inner ends of the retorts is characteristically a vertical lattice work of refractory blocks, but may be a middle wall, with ledges as in the Belgian furnace. The retorts have the cross-section like a chain link, are about 12 in. high inside, and hold about 34 kg. of charge. The condensers are larger and longer than in the Belgian furnace. The front of the furnace is divided into closets completely enclosing the condensers, one closet comprising six condensers. The closets are subdivided by three horizontal shelves, which have holes through which the residues raked out of the retorts are dropped into pockets below the working floor.

As thus defined, the Rhenish furnace has the main design of the Silesian, and obtains much of the economy of the latter in labor and fuel, but it has the suspended retorts of the Belgian, giving the advantage of better heating. The dimensions of the retorts are a compromise between those of the Belgian and the Silesian and are as large as is consistent with the successful treating of high-grade ore, for reasons previously stated, and as long as will permit the load safely to be sustained. However, the retorts themselves are not a distinguishing feature of the Rhenish furnace, for the same retorts may be used in a Belgian furnace without destroying the distinct characteristics of the latter.

The Belgian furnace itself has undergone great modifications which have resulted in some confusion of description. The American zinc smelter in speaking of the Belgian furnace means the small, direct-fired blocks installed at Pittsburg, Kan., and vicinity about 50 years ago and still used there within a year or two. The gas-fired furnaces used in the more modern plants he calls "Hegelers" or "Siemens." A correct description would be "Old Belgian," "Hegeler-Belgian" and "Siemens-Belgian." The Hegeler-Belgian is simply a very high, gas-fired Belgian, turned over on its side. The Siemens-Belgian is an elongated Belgian, which was rendered possible by its method of gas firing. Besides such modifications the Belgian furnace may be equipped with either cylindrical or elliptical retorts, or even the large retorts employed with the Rhenish furnaces. Thus, the last were installed in the original Siemens-Belgian furnaces in this country, but their use did not endure.

The distinguishing features of the Belgian furnace are the use of rather small retorts, arranged in four or five rows, each retort bridging from front wall to back wall (or middle wall in the case of a double furnace); but especially the design of the front walls. These are thin, being scarcely more than sufficient to support the front ends of the retorts. Outside of the front walls the structure is supported by an iron *devanture* of only small depth, the main function of which is to iron the furnace, while the horizontal shelves merely support the condensers and aid in clearing out the retort residues. Thus the front of the furnace is latticed off in a series of shallow pigeon holes instead of the deep closets of the pure Rhenish furnace.

Differences in Practice.—The differences in fronts create a rather important difference in metallurgical operation. We used to deplore the necessity for making the front wall of a distilling furnace so thin, which we thought resulted in a terrific waste of heat by radiation. We learned, however, from thermal computations that this radiated heat was necessary in order to keep the condensers

at the proper temperature, which computations received an illuminating confirmation in some electric furnace smelting when it was found necessary to arrange an independent fire under the condenser. In the Belgian furnace the condensers stick right out from the front wall of the furnace and it is more difficult to regulate their temperature than it is in the Rhenish furnace wherein they are enclosed in closets, which often have adjustable, sliding doors in their fronts.

However, as I have previously indicated there are all kinds of departures from typical Rhenish design and practice. Thus, at Blende, Colo., the furnaces built originally as Welzers (Overpelt-Rhenish) have been greatly modified. While these furnaces have the deep closets they are now divided by iron plates instead of firebrick tiling. The condensers fit fully into the mouths of the retorts and of course have to be taken down during the maneuver. The discharging at Blende is now done by means of a machine, which demands free access to the retort, anyhow.

European zinc-distilling practice has concentrated rather emphatically upon the Rhenish type of furnace, to which the Silesian smelters have been going over in recent years. This type of furnace gives as good zinc extraction as the Belgian, is more durable both as to retorts and as to furnace itself, and lends itself to infrastructures that aid in producing rather better economy of fuel than is realized with the Belgian furnace of Europe. They do not, however, excel the best regenerative Belgians of the United States, although they equal them. In replacing broken retorts it is more trying on the men to handle and insert the heavier Rhenish retorts than it is the lighter Belgians, but on the whole the labor in operating the Rhenish furnace is rather less and is distinctly easier than the Belgian. Nevertheless the Rhenish furnace, which has had only one prolonged trial in the United States, has found no favor here, and American smelters in adhering to the Belgian type stick to the old cylindrical retorts, although the Belgian smelters themselves use generally the elliptical. There are reasons for this difference in ideas but present limitations do not permit a discussion of them.

Zinc-lead Smelting.—Until about 20 years ago zinc smelting was conducted purely as a method of extracting zinc. The zinc smelter did not want to have lead in his ore and penalized it. With the advent of the great supplies of Australian ore, however, and other ores of similar character the zinc smelters of Europe, especially of the Continent, overcame their aversion to lead and indeed began to demand its presence to an extent of about 6 per cent as a minimum. They had learned that lead did not prejudice the distillation of zinc except in so far as it contaminated the spelter, which was no very serious matter. Zinc-smelting in Europe was therefore put practically upon a zinc-lead basis. The same thing was done by numerous smelters in the United States, but not to the same extent as in Europe.

In distilling an argentiferous and plumbiferous zinc ore some of the silver and lead go over into the spelter, but the major parts remain in the retort residue. The latter may be passed to the lead-smelting blast furnace, or it may be subjected to mechanical concentration and the concentrate alone be smelted for argentiferous lead. When concentration is done some of the surplus reduction coal is recovered. The choice of the method is determined by costs. Europeans generally concentrate; Americans smelt directly. The ultimate extraction of lead and silver from a zinc ore is about 50 to 75 per cent of the original contents, 62.5 per cent being perhaps a fair average.

Another method of treating zinc-retort residues is to burn them in Wetherill

furnaces for the production of zinc oxide, either as a pigment or as an impure product to be returned to the distilling furnaces. The surplus coal in the residues is usually sufficient for the execution of this process, which serves to extract about five-eighths of the zinc remaining in the residues, when the latter assay about 7 per cent Zn. This process is used extensively by American smelters, who owing to their low-temperature distillation have richer residues than occur in good European practice. If the residues contain much silver this process would be inadvisable for the silver would largely be lost.

The electrothermic smelting of zinc ore need be referred to but briefly, for only in Scandinavia has it become a commerical art. The metallurgical principles of zinc distillation obtain in electrothermic smelting just as they do in the ordinary pyrometallurgy. There are two large plants in Scandinavia, viz. at Trollhattan in Sweden and at Sarpsborg in Norway. Besides these, there are one or two small plants. A new plant is being built at Glomfjord. This is to have capacity for smelting 60,000 metric tons of ore per annum. At the end of 1921 it had not been completed, but construction was well advanced. The electric furnaces used for ore smelting in Scandinavia are resistance furnaces, and are designed and run as combined zinc and lead smelting furnaces, both zinc and lead being obtained in the same operation, the gangue of the ore being fluxed and drawn off as slag.

In the smelting at Trollhattan until within a year or two the idea was to condense spelter directly from the distillation furnace. In so doing there was experienced the common difficulty in the matter of condensation, an unduly large proportion of the zinc being condensed as blue powder. We know now that that is inherent to any zinc ore reduction and distillation process that is carried on continuously. The common process is conducted intermittently and in stages. In the first stage there is an expulsion of oxidizing gases. After they have been driven off, and when the effluent gas becomes essentially carbon monoxide the temperature of the furnace is raised to the point of zinc reduction and distillation, and in such an atmosphere condensation of the zinc mainly as spelter can be effected. In a furnace operated continuously there can be no such control of gaseous conditions, and as fresh ore is charged into the furnace there is a constant development of oxidizing gases, and coincidentally there is more or less dusting. The entrainment of mechanical dust with the stream of gas and vapor constitutes an additional condition adverse to condensation as spelter. The continuous reduction, distillation, and condensation of zinc (as spelter), requires therefore the conditions of a two-stage operation, just as there is in the common pyrometallurgy. With a continuously operating furnace there must be either a preliminary stage of pre-reduction in another furnace, or there must be a subsequent stage of blue powder retreatment, also in another furnace. Whichever be the choice, there are two stages or two steps.

The Trollhattan metallurgists adopted the method of (1) reduction and distillation and (2) blue powder retreatment. The latter was done by redistillation in an electric furnace, but this was found to be unduly expensive. The discovery was then made that the blue powder could be melted down in a comparatively inexpensive way if subjected to heating to the melting point of zinc and at the same time to a rubbing action.

In the new process recently developed at Trollhattan, which is also to be

applied at Glomfjord, the resistance furnaces are run at high temperatures, the lead being completely volatilized and no attempt being made to condense the zinc as spelter. The furnace is operated on the principle of producing a highly siliceous slag, which commonly contains about 50 per cent of silica, and creates conditions favorable to a high degree of zinc expulsion, *i.e.* the percentage of zinc scorified and retained by the slag is relatively small. The vapor is rapidly cooled, the metals condensing as powder, which is subsequently melted down, affording a very leady spelter, which is finally refined by redistillation in an electric arc furnace, but of course an ordinary grade of spelter can be produced by simple gravity refining. The ore smelting furnaces have now been built and successfully operated for large capacity, as much as 12,000 kg. of ore per 24 hours being smelted in a simple furnace. This in itself is an achievement beyond what anyone else has accomplished in this field and is to the credit of the Swedish metallurgists.

Hydrometallurgy.—The extraction of zinc by purely hydrometallurgical methods has never attained any great importance, indeed scarcely anything but occasional application. Owing to the formation of insoluble zinc ferrite during the roasting the extraction of zinc is apt to be disappointing. Given a sulphate solution, white vitriol (zinc sulphate) may be obtained as a commercial product by evaporation and crystallization as used to be done in the Lower Harz, Germany, but the market for that product is limited. However, such sulphate solutions may be, and are, used for the production of lithopone by precipitation with barium sulphide. To obtain zinc oxide from a zinc sulphate solution is difficult, but it was once done on a commercial scale by the Parnell process, which was based on the reaction between zinc sulphate and zinc sulphide when heated in a muffle furnace.

Hydro-electrometallurgy.—The electrolytic production of zinc, which has now become a great commercial art, is based upon the ordinary hydrometallurgical steps up to the point of obtaining a purified solution of zinc sulphate. The same difficulties of obtaining a satisfactory dissolving of the zinc obtain here, but need not be insuperable for the lixiviation residues may be burned in Wetherill furnaces, or reverberatory furnaces, for the expulsion of the zinc that they retain. There are the other difficulties, such as result from gelatinization of silica, reprecipitation of zinc, etc., that are to be expected in a hydrometallurgical process. They are minimized by starting with a relatively pure ore. One of the factors contributing to the success of electrolytic zinc extraction during the last 5 years, whereas all attempts for 25 years previously had been failures, is that the flotation process gave us a relatively clean, high-grade ore, whereas previous work had been done on low-grade, impure run-of-mine ore.

The essential conditions for successful electrolytic deposition of zinc are purity of anodes (lead,) cathodes (aluminum) and electrolyte (solution of zinc sulphate), and by purity is meant not merely relative purity but a high degree of it. Some foreign elements, the alkalis for example, may be present with impunity, others such as manganese may even be desirable, but others, such as cobalt, are poisonous even if present only to the amount of a few hundredths of a per cent. Consequently, after the solution of zinc has been obtained it must be purified by the precipitation of objectionable elements. This is an essential and often a troublesome part of the process. Iron is converted to the ferric state by the manganic acid, or acid salts, that are

present and is precipitated by lime. Copper and cadmium are thrown down by zinc. These operations are relatively simple, but not so the removal of chlorine and cobalt. However, the electrolysis of a solution that is not refined quite so much as it ought to be may be aided by the addition of glue.

The vats are commonly arranged in cascades. The electrolyte is introduced into the head cell made up to about 60 g. zinc and 25 g. free acid per liter. A difference of 3.6 volts in potential and a current density of 25 amp. per square foot are common practice. In its passage through the cascade the solution heats. Its temperature is advisedly controlled by means of cooling pipes interposed between the cells. With the gradual peroxidation of the manganese the electrolyte assumes a deeper and deeper pinkish hue. Finally it issues from the last cell with a zinc content of about 30 g. and an acidity of about 75 g. per liter, and is returned for the lixiviation of a fresh charge of ore. The leaching is commonly done in Pachuca tanks; the separation of residues and the filtration of the solution by means of Dorr classifiers and Oliver filters. The mechanical arrangements, the difficulties and the limitations of the hydrometallurgical part of the process are similar to what obtain in any process of that character. The arrangement of the electrolytic tank room is similar to that of a copper refinery. In zinc electrolysis, however, the liberation of an acid mist is considerably more objectionable.

Rotating cathodes have certain theoretical advantages. They were tried in the Judge plant at Park City, Utah, but they did not develop satisfactorily. However, such cathodes have been used in the electrolysis of zinc-chloride solution according to the Hoepfner process. In that process, which has been applied on a small scale at Führfort in Germany and at Winnington in England, chlorine is liberated at the anode and is conducted away for the manufacture of bleaching powder.

In good practice in zinc electrolysis there is a deposition of about 10 lb. of zinc per horsepower per day. At $30 per horsepower year this is about 0.8 ct. per pound of zinc. The other costs—for leaching, purifying, melting, etc.—raise the total per pound of zinc to a high figure, which must be offset by superior advantages in other respects, such as superior extraction of zinc, lead and silver. The conditions under which cheaper power and offsetting advantages exist are rather rare and consequently electrolytic zinc extraction is hardly to be expected to become a process of universal application, or likely to displace distilling, although the production of electrolytic zinc has had and will continue to have a profound effect upon commercial conditions. Already it has destroyed the historic large premium for high-grade zinc.

METALLURGY OF LEAD

By Walter Renton Ingalls[1]

The art of extracting lead from its ores is based on these principles: (1) the reduction of lead oxide by carbon, or carbon monoxide; (2) the reaction between lead sulphide and lead sulphate or oxide, resulting in a double decomposition with the formation of lead and sulphur dioxide; and (3) the decomposition of lead sulphide by metallic iron. All of these reactions are endothermic, *i.e.*, they absorb heat, which must be supplied extraneously. The first principle is the basis of what is known as the roast-reduction method of smelting, in which lead oxide (or lead silicate, or some other oxidized compound) must be prepared from sulphide ore by a preliminary roasting. The second is what is known as the roast-reaction method. And the third is the basis of the precipitation method.

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All of these methods are employed practically in the United States at the present time, either alone or in combination, the latter being most commonly the case; also, the principles are not practically so sharp as theoretically stated, the reactions fundamental to one process invariably playing a certain part in the other processes.

If a lead ore were absolutely pure, there would be no other consideration in the smelting processes than those reactions which relate to lead and its chemical combinations; but practically lead ores are never pure, the valuable minerals being mixed with a certain proportion of foreign matter, which must be separated by making a slag of it. In the roast-reaction method of smelting, it is true, no slag properly speaking need be made, the reduced lead being liquated out from the worthless impurities, but the latter will still retain a high percentage of lead, and in order to effect a high degree of extraction from the ore it must be subjected to a further smelting process in which a true slag is made. In making a slag, the object is to combine the impurities into a fusible silicate, which when molten will be of comparatively low specific gravity, so that the heavier lead will settle to the bottom of the crucible of the furnace, whence it may be drawn off separately, while the lighter slag will float on top. Besides the slag and metal, there is formed practically another substance, called matte, which is lighter than the metal but heavier than slag. Matte is an artificial sulphide, consisting in lead smelting usually of the sulphides of iron, lead, and copper (if copper be present in the ore), and owes its origin to the incomplete elimination of sulphur from the ore. Similarly, speiss is an artificial arsenide of iron.

The difference between lead smelting in principle and in practice is chiefly due to the incompleteness with which the basic reactions are carried out, and the qualifying effect of the impurities that are commonly met with in ores. Thus certain metallic impurities are reduced with the lead, contaminating it and necessitating a subsequent refining process. Other impurities affect the composition of suitable slags. Others affect the running of the furnace in various ways. It is the reconciliation and neutralization of these various difficulties that constitute the duty of the metallurgist, whose purpose is to treat a ton of ore in such way that the difference between the value of the products extracted and the expense of treatment will be the maximum, the value of the products depending largely upon the percentage extracted, and the expense of treatment including interest and amortization charges on the capital invested in plant, etc.

The most primitive form of lead smelting in the United States was practiced with the log and ash furnaces in Missouri prior to 1850. They employed the roast-reaction system of smelting and were applicable only to non-argentiferous galenas, of very high grade in lead. They were for the most part displaced about 1840 by the Scotch[1] hearth furnace. Later on reverberatory furnaces of the Flintshire type came into use, but never extensively, nor with such success as to develop a permanent metallurgical practice. The Scotch hearth, however, has survived, and in its modern development is the basis of a highly efficient process in the treatment of certain classes of ore, especially high-grade non-argentiferous galena.

Neither the Scotch hearth nor the reverberatory furnace is well adapted to the treatment of argentiferous ore, or to the treatment of ore containing less than 60 per cent of lead, while the smelting of carbonate ores alone in these ways is of course

[1] This term is not strictly accurate, since the furnaces of this class that were introduced into America were early modified materially from their prototype as employed in Great Britain. They are described more precisely as the American-Scotch hearth, which term is to be found in many metallurgical treatises, but is never heard in practice, the term Scotch hearth having been adopted for brevity.

infeasible. For these reasons, by far the major part of the world's lead is produced by smelting in the blast furnace.

In the early history of blast-furnace smelting of silver-lead ore in the United States, the work was done chiefly for the reduction of the ore of a single mine, or single group of mines, as at Eureka, Nev., Cerro Gordo, Cal., and at several places in Utah. The charges were generally rich in lead. Their silver and gold contents went of course chiefly into the lead, but although they were commonly the most important elements of value in the ore, the process was essentially one of lead smelting.

Later on, when many of the rich lead deposits became exhausted, when the tonnage of rebellious[1] gold and silver ores greatly increased, when transportation facilities had been largely improved, and when the smelting industry had become concentrated in a comparatively few centers, drawing ore supplies from numerous districts, the average percentage of lead in the ore smelted fell to a low figure, and although in the aggregate the production of lead increased immensely the process of reduction became essentially one of gold and silver smelting, the lead in the ore functioning as collector of the precious metals and being viewed metallurgically from that standpoint.

Subdivisions of Lead Smelting.—It is useful, therefore, to consider the art of lead smelting in its present development as being divided under three heads, *viz.*:

1. Reduction of non-argentiferous galena, in which all the methods of smelting are applicable, if the ore be sufficiently rich in lead.

2. Reduction of special classes of argentiferous ore, the product of one mine or a few mines, in which the blast furnace only is advisable. The character of the charge and the bullion are chiefly dependent upon the composition of the ore, while the slag is governed by the composition of the ore and the availability of the necessary fluxes and may vary within rather wide limits.

3. Reduction of general mixtures of argentiferous ores, the product of many mines. The most important part of the present lead-smelting industry falls under this head. The ores are mixed to make a slag of definite composition and a bullion of nearly uniform grade, which vary only within narrow limits. The percentage of lead in the composite ore, *i.e.*, the furnace charge, is comparatively low, and is designed to be only what is necessary to collect the gold and silver most efficiently. To improve the collection of gold and silver a proportion of copper is generally added to the charge, which results in the production of a leady cupriferous matte as a between-product.

The third system is essentially gold and silver smelting on a lead basis, and is commercially analogous precisely to smelting on a copper basis. These two kinds of smelting are indeed competitive, the same ores being to a large extent amenable to treatment in either way. However, the copper smelter is not desirous of receiving lead-bearing ores, while the lead smelter needs a certain proportion of copper-bearing ore. In the treatment of mixtures properly compounded, smelting on a copper basis is more profitable than on a lead basis, and the tendency of metallurgical practice during the last 10 years has been toward its adoption wherever feasible. The two kinds of smelting are now to be witnessed in operation at the same places, and even side by side in the same works (*vide* Salt Lake City, Utah; Aguas Calientes, Mexico, and elsewhere). The successful collection of lead fume from the copper converter blowing leady matte has made some copper smelters less averse to lead in their ore than they used to be.

[1] This word when applied to gold and silver ores indicates those of a character not readily amenable to the milling processes.

In smelting any kind of lead ore in any way, the sulphur must be burned off, partly at least, and the impurities must be combined in a slag, fusible at approximately 1,100 to 1,200°C., and of specific gravity not to exceed 3.6, or but little more. The slag must be of a composition which will form at the right point in the smelting process, will be thoroughly liquid, in order to insure a satisfactory separation from the matte, and will require the minimum consumption of fuel, the chief part of which in blast-furnace smelting is always consumed in effecting the formation of the slag. A good slag will cause the charge of ore and flux to descend evenly and regularly in the furnace, avoiding the formation of accretions in the hearth or on the walls, keeping the lead in the crucible red-hot and preventing any creeping up of the fire and the ensuing danger of loss of lead and silver by volatilization.

The sulphur is eliminated in various ways, which may be enumerated as follows:

1. *Roasting.*—Performed usually in hand-raked reverberatory furnaces with a single, long hearth. Bruckner cylinders are also employed, but most of the other forms of mechanical furnaces are inefficient because of the stickiness of lead ore in roasting, wherefore the attempts to apply them have been generally abandoned. Lead ores, being usually low in sulphur, are not self-burning in the ordinary roasting furnace, and decomposition of lead sulphate being effected only by reaction with silica, forming lead silicate, the necessary temperature must be chiefly supplied by the combustion of carbonaceous fuel. In good practice the consumption of coal (Colorado bituminous and other western grades) is about 30 per cent of the weight of the ore roasted. The roasting of lead ore may be done in three ways, *viz.:*

(*a*) Ordinary roasting, in which the ore is simply desulphurized, at the same time being more or less sintered. Often the ore is partially fused, so that upon withdrawal from the furnace it crusts or may be pounded into cakes, which may be called "sinter-roasting."

(*b*) Slag roasting, in which the ore is completely fused.

(*c*) Blast roasting, a recent improvement, which will be discussed more fully further on.[1]

Slag roasting is performed in modifications of the ordinary reverberatory furnace, designed so as to permit the maintenance of a suitably high temperature at the discharge end.

It is objective in roasting to reduce the sulphur as low as possible, without entailing undue losses in other directions, since it is reckoned roughly that each unit of sulphur remaining in the ore increases the cost of smelting 25 cts. per ton (under pre-war conditions) The sulphur is more completely eliminated by sinter roasting than by ordinary roasting, and more completely by slag roasting than by sinter roasting, but at the same time the loss of lead by volatilization is heavily increased and in slag roasting is so high that the process has been abandoned in the United States, save in one or two instances, while sinter roasting has had no wide practice, and ordinary roasting, by which the sulphur is reduced to about 4 per cent, had become the generally adopted method until recently displaced by the "blast-roasting" process.

2. *Roast Reaction.*—Lead sulphide burned partially to sulphate reacts with undecomposed sulphide, setting free metallic lead and sulphur dioxide. This process is effected in the reverberatory smelting furnace (Flintshire, Tarnowitz, etc.) wherein the

[1] See page 820.

charge is first partially roasted and the reaction is then effected under increase of temperature; also in the Scotch hearth, wherein the roasting and reacting go on contemporaneously. In the modern blast furnace, which has lines and is operated under conditions promoting oxidation, roasting and reacting play an important part.

3. *Precipitation.*—In this method the ore is charged raw into the blast furnace and the lead sulphide is decomposed by iron, precipitating metallic lead, while the sulphur combines with the iron, forming a matte, from which the sulphur is subsequently eliminated by roasting. The quantity of matte to be roasted is apt to be as much as the quantity of ore smelted, but the loss of lead is less than if the ore were roasted originally. There are other drawbacks, however, and this method which has never had any wide application in the United States is now employed by itself in only one or two instances, if at all. The reaction takes place to some extent in any blast furnace, however, and it together with the reaction between the sulphide and sulphate described under the previous caption is largely relied on in modern practice, wherein galenas of high grade in lead are commonly charged raw into the blast furnace to save the comparatively high loss of lead which is inevitably suffered even in ordinary roasting. Precipitation smelting may also be done in the reverberatory furnace, but that method is quite inefficient and has seldom been practised either in America or Europe.

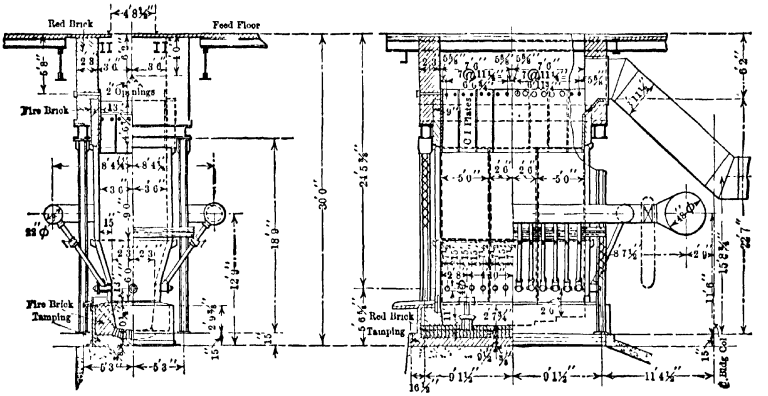


FIG. 3.—Blast furnace, International Smelting Co., Tooele, Utah.

After elimination of sulphur by ordinary roasting or by blast roasting, the ore is ready for smelting in the blast-furnace. Naturally oxidized ores go of course to the blast furnace without any preliminary treatment, save breaking to the proper size.

The function of the blast furnace is to reduce the metal and slag the impurities so that a separation can be made. This separation is effected by the difference in specific gravity of the various products. The specific gravity of liquid (molten) lead is about 10.5; that of matte ordinarily ranges from 4.5 to 5. In order to insure a satisfactory separation of matte and slag, therefore, the specific gravity of the latter should be at least one degree lower than the lightest matte. Both the matte and the slag must be thoroughly liquid at the temperature of issue from the furnace. Consequently the matte must be free from components which make it mushy, like zinc, and the slag must be of a composition which is easily fusible at 1,100 to 1,200°C. The cleanness of the slag, *i.e.*, its freedom from gold, silver, lead, and copper, is dependent chiefly on these physical conditions. The

lead content of a good slag should not exceed 1 per cent; the silver content should not exceed 0.8 oz.; the gold content should not be more than a trace. In order to achieve such a result the specific gravity of the slag should not be more than 3.6, and it should be of approved chemical composition.

In making a slag, the metallurgist is practically limited by the elements which commonly occur in ores, and to cheap fluxes like limestone. The commercial slag is a silicate of two or more bases. The fundamental constituents are silica, iron, and lime. The iron may be replaced to some extent by manganese, and the lime to some extent by magnesia, zinc, and baryta. These elements ordinarily constitute 90 per cent of the slag. The remainder is chiefly alumina, barium sulphate, soda, and potash, etc. In preparing the furnace charge, a mixture of ores and fluxes is made in such proportions as to produce a slag of the desired composition. In lead smelting the permissible range in silica content is rather narrow, varying from 28 to 36 per cent, and ordinarily also the percentages of ferrous oxide and lime range only within narrow limits, the percentages stated nominally as ferrous oxide and lime including their equivalents respectively of manganese oxide and magnesia or zinc oxide.

The efficiency of the lead-smelting process depends chiefly upon (1) the method of sulphur elimination, affecting the cost of the operation, the loss of gold, silver, and lead, and the physical condition of the product delivered to the blast furnace; (2) the design and construction of the blast furnace and its accessories, the method of operation, the physical condition of the material charged, the correct composition of the slag, the character of the bullion produced and the means to collect dust and fume; (3) the means for handling products throughout the process.

The better the character of the slag, the faster will be the running of the furnace, *i.e.*, the greater the quantity of charge smelted per square foot of hearth area,[1] and the lower the loss of lead and silver in the slag and in the fume. The lower the proportion of very fine ore in the charge, the faster will be the running of the furnace and the smaller the percentage of flue dust to be collected and rehandled. The better the character of the bullion, the less irregularity in the management of the furnace and the less the cost of refining. A detailed consideration of all of these governing and largely interdependent factors is impossible in a brief statement of the principles of the art as developed in modern practice, but such will be found in the standard treatises on the subject. It is aimed here to emphasize the predominant effect of the slag character, *i.e.*, the make-up of the furnace charge, in determining the cost and efficiency of the smelting process. It may also be said that the successful development of the silver-lead smelting industry hinged upon this matter. As the histories of the various lead-smelting districts are examined, it will appear strikingly how the process was quickly made successful in those which had the advantage of a self-fluxing ore, like Eureka, Nev., and how it was struggled with in many other districts, and how, as lead smelting became a well understood art, it came to be recognized that an assured and adequate supply of the right classes of ore was the fundamental prerequisite for the inauguration of a successful business.

Given supplies of silica, iron, and lime, there is no difficulty in producing a slag of any desired composition, but the smelting might be so costly as to be unprofitable. The cost of smelting is properly based on the charge, *i.e.*, all of the material except fuel which is put through the furnace. It is the aim of the metallurgist to have the ore in the charge at the maximum possible percentage, *i.e.*, it is sought to obtain all of the necessary fluxing elements in a proper proportion in the ores purchased for smelting, since the time, fuel, and labor required to smelt a pound of flux are the same as for a pound of ore, and for each pound of flux put into the charge there is one pound less of ore. It is consequently of the utmost importance to the smelter to be able

[1] The hearth area is the horizontal section of the furnace on the line of the tuyeres.

to secure ores that upon mixture will contain the proper proportion of slag-forming substances and will obviate the necessity of making up the proper proportion by the addition of barren fluxes. It is seldom possible to attain the acme of that condition, a small proportion of lime-rock having usually to be added to the charge while there is always a certain quantity of foul slag, flue dust, roasted matte, and other between-products that must be added to the charge; but in the modern American practice of silver-lead smelting the ore in the charge amounts usually to 80 per cent or more.[1]

The price which a smelter will give for any particular ore is consequently determined by his fluxing requirements and the supply of various kinds of ore on hand or offered. The smelter refers to the difference between the cost of a ton of ore and the proceeds which he obtains from it as the "margin," out of which he has to pay the cost of smelting, the remainder of the margin being his profit. The margin varies greatly according to the class of ore treated and the profit is dependent upon the average; consequently it is sought to smelt as much "high-margin" ore as possible.

As a simple illustration, suppose there were available two kinds of ore, *viz.*, a lead-carbonate ore, containing 22.5 per cent lead, 20 per cent ferrous oxide, 4 per cent lime, and 27 per cent silica; and an argentiferous iron ores, containing 60 per cent ferrous oxide, 4 per cent lime, and 25 per cent silica; and lime-rock containing 1 per cent ferrous oxide, 50.5 per cent lime, and 8 per cent silica. Suppose it were desired to mix these ores so that the slag would have the composition 34 per cent silica, 34 per cent ferrous oxide, and 17 per cent lime, it would be necessary to add to each ton of the lead ore 0.25 ton of iron ore and 0.25 ton of lime-rock. The mixture would contain 15 per cent lead. In the daily charge of a furnace, say 150 tons, there would be 100 tons of lead ore, 25 tons of iron ore, and 25 tons of lime-rock. Assume the cost of smelting to be $\$3.75 \times 6 \div 5 = \$4.50$. In order to realize a profit of \$1 per ton, assuming that the full value is paid for gold, silver, and lead, the smelter must have a margin of \$5.50 per ton. But suppose the iron ore is so low in silver that it will not stand a treatment charge of more than \$2 per ton, the smelter obliged to have it as a flux must make up the deficit by an increased charge on the lead ore, which then would have to be \$6.37½.

This illustration shows also what advantage it would be to the smelter if he were able to substitute for the lime-rock an ore of similar content in lime, on which he could make a treatment charge. It shows also the advantage of making a slag as siliceous as possible, which enables the maximum percentage of the usually profitable siliceous ore to be carried in the charge.

The foregoing analysis of the commercial principles of lead smelting relates especially to the conditions involved in the operation of a custom smeltery, supplied by ore from numerous mines, in which the percentage of lead in the aggregate is comparatively small, the business being conducted not with the particular view of producing lead, but rather with that of smelting a large tonnage of ore. Nevertheless the same fundamental principles govern the smelter of the product of a single mine, or group of mines, although he may be more constrained in the matter of ore mixtures; and also the smelter of high-grade galenas, who may extract directly a large proportion of the lead in Scotch hearth or Flintshire furnaces, but is still obliged to effect the final separation of the gangue by smelting the gray slag in a blast furnace.

[1] This means 80 per cent or more of the charge, exclusive of the slag which is used in larger or smaller quantity, often rather large, to facilitate the running of the furnace. Great efforts are made to eliminate this "side-charge" but it does not appear possible to do so.

The practice of the metallurgy of lead has resolved itself at the present time into smelting in the blast furnace for argentiferous ores and smelting in the Scotch hearth for non-argentiferous ores. In both kinds of smelting the smoke and fume are filtered by means of baghouses, the use of which has greatly reduced the loss of lead. In silver-lead smelting the loss of lead has been further reduced by the introduction of the blast-roasting process, which has eliminated the large loss that was formerly incurred in roasting in reverberatories. The result of these

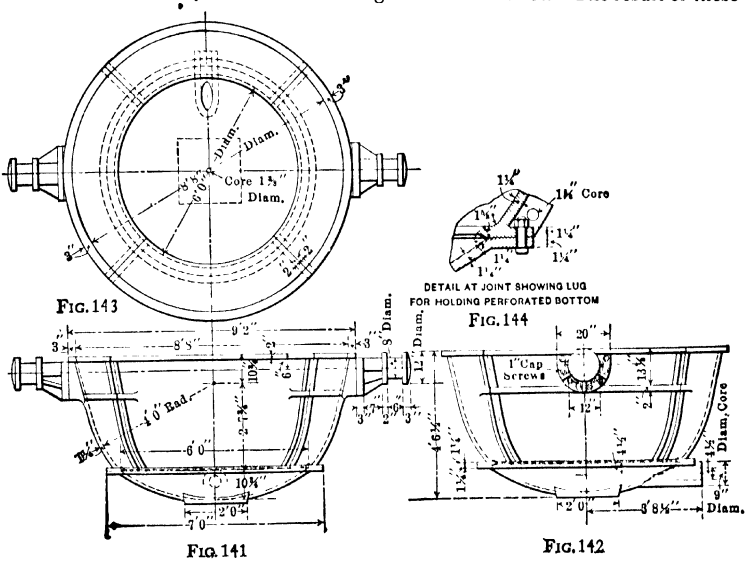


FIG. 8.—Sectional cast-iron pot for blast roasting.

improvements has been to make it possible to extract 95 per cent of the lead in smelting silver-lead ores in the blast furnace and 98 per cent in smelting high-grade galena in the Scotch hearth. The two methods of smelting are applied under radically different conditions. In silver-lead smelting a prime function of the lead is to act as collector for the precious metals. The percentage of lead in the charge is ordinarily low, say about 10 per cent, but there are regions where the main supply of ore is galena and in those regions the furnace charges are commonly much higher in lead. In any case the proportion of slag to ore that is made is much higher than in the treatment of high-grade galena ore in the Scotch hearth and consequently loss of metal in the slag is higher. The Scotch hearth method of smelting has been confined to the treatment of non-argentiferous galena containing 60 per cent of lead, or upward. This method of smelting has been improved by the introduction of the Newnam mechanical rabbler, which has reduced and ameliorated labor conditions, an important thing in view of the severity of the latter, especially in hot weather.

Except at Port Pirie, South Australia, the metallurgy of lead is technically less advanced than in the United States and Mexico. Spain, which is one of the four great lead-producing countries of the world, is distinctly backward. It is probable that the Spaniards, in revising their metallurgy, will adopt American methods.

ROASTING

By F. R. Pyne[1]

Definition.—Roasting is the heating to an elevated temperature, without fusion, or at most to incipient fusion, of ores or metallic compounds in contact with oxidizing, reducing or chloridizing materials, in order to produce a chemical change or to eliminate a component by volatilization. It is a preliminary step to many metallurgical operations, the usual object being partially or completely to eliminate sulphur, arsenic, antimony, or other readily volatile constituents, such as carbon dioxide, which may interfere with subsequent processes.

Types of Roasting.—Roasting may be divided into three principal classes: oxidizing, reducing, and chloridizing. In the oxidizing roast the operation is performed by heating with excess of air to such a temperature that the affinity of the undesirable element for oxygen becomes stronger than for the metal with which it is associated. In the reducing roast an oxidized metallic compound is heated in the presence of a strong reducing agent, such as carbon, to a temperature sufficient to cause the deoxidization. In the chloridizing roast the object is to convert the metallic compounds into chlorides by treatment with chlorine gas or chlorides.

The most common and important type of roast is the oxidizing roast of metallic sulphides. When a metallic sulphide is heated to a sufficiently high temperature with access of air, there is formed sulphur dioxide and a metallic oxide:

$$2MS + 3O_2 = 2MO + 2SO_2$$

The temperature, in degrees Centigrade, at which the leading metallic sulphides ignite is shown by the following table.[2]

Material	Size of grain, millimeters		
	1	1–2	Over 2
Pyrite	325	405	472
Pyrrhotite	430	525	590
FeS	..	535	
Ni 73.3 S 26.7	700	802	886
Co 66.37 S 33.63	574	684	859
Co 70.20 S 29.80	514	751	1,019
Stibnite	290	..	340
Molybdenite	240	..	508
Cinnabar	338	..	420
Chalcocite	430	..	679
Bi. 83.3 S 16.7	500	..	626
Mn 61.01 S 37.98 Fe 2.02	355	..	700
Argentite	605	..	875
Blende	647	..	810
Galena (in oxygen)	554	..	847
Millerite	573	.	616

[1] Works superintendent, U. S. Metals Refining Co., Chrome, N. J.

[2] Hofman, "General Metallurgy," p. 404.

Proper oxidation requires a temperature sufficiently high to produce the necessary affinity between the oxygen and the sulphur, but it must not be so high as to cause the surface of the particles of ore to melt and form a protecting layer which retards the oxidizing action and may even cause it to cease. This temperature may be obtained by the combustion of extraneous fuel or by the heat of oxidation of the constituents of the charge.

A second requirement for proper oxidation is a constant and abundant supply of air in immediate contact with the surface to be oxidized. The necessity for an abundant supply of air is due to the fact that the oxidizing power of the air is lowered out of all proportion when diluted. In other words, if the air for oxidization is diluted with its own volume of gaseous furnace products, the oxidizing effect of the resulting mixture will be much less than half the oxidizing power of pure air. Therefore, the more rapidly the gaseous furnace products are removed and replaced by pure air the more rapid will be the roast.

The speed and thoroughness of the roast are also governed by the size of the particles. It is obvious that the finer the ore is crushed the greater will be the surface exposed to the oxidizing influences. As fine crushing always results in losses by handling, flue dust, etc., it will be seen that there is an economical point when the advantages gained by the increased speed of roasting are balanced by the dust losses which necessitate expensive recovery systems. The usual charge of ore to the roasters consists of coarse and fine particles, and the latter will be thoroughly roasted long before the former and to obtain a dead roast requires extensive stirring and heating. But should only a partial elimination of sulphur be desired, as in copper smelting, the roast is carried to a point where the over roasting of the fines balances the under roasting of the coarser particles, so that the final mixtures give the desired sulphur content.

Sulphatizing Roasting.—The gases produced are more or less rich in SO_2, depending upon the amount of air furnished per unit of material, and in the presence of contact substances the SO_2 may be converted into SO_3

$$SO_2 + O \rightleftarrows SO_3$$

The SO_3 formed may combine with metallic oxides to form sulphates

$$MO + SO_3 \rightleftarrows MSO_4$$

In some types of roasting the aim is to produce a maximum amount of sulphates, in which case the operation is known as a sulphatizing roasting. The amount of SO_3 present in the gases and the existing temperature determines the formation of the sulphates. The reaction is a reversible one depending upon the temperature and pressure of the SO_3.[1] The following table taken from Fulton's "General Metallurgy," page 218, gives the equilibrium conditions for temperature and pressure of SO_3 for several sulphates.

[1] I have some doubt as to whether this matter of temperature range in the formation and decomposition of sulphates in roasting is so simple as it is usually represented. There is much more experimentation needed to clear the subject, but I am inclined to believe, from some experimental evidence in my possession, that varying ratios of water vapor to the sulphur trioxide present profoundly alter the rate of formation of sulphates and the quantity formed. Air conditioning may yet be considered an essential for the proper control of sulphatizing roasting.—EDITOR.

Fe_2SO_4 $Fe_2O_3 + SO_3$		$Al_2(SO_4)_3$ $Al_2O_3 + SO_3$		$2CuSO_4$ $2CuO{\cdot}SO_3 + SO_3$		$2CuOSO_3$ $2CuO + SO_3$		$ZnSO_4$ $ZnO + SO_3$	
Temperature	Millimeters	Temperature	Millimeters	Temperature	Millimeters	Temperature	Millimeters	Temperature	Millimeters
553	23	572	28	546	43	600	62	675	5
570	33	621	51	588	55	653	98	690	6
592	45	681	120	615	70	686	123	720	24
614	70	702	180	642	98	705	139	750	61
634	113	720	261	665	130	728	173	775	112
650	149	731	356	700	233	745	209	800	189
660	182	742	480	714	324	775	298		
680	286	748	692	725	460	805	542		
690	401	...	...	731	647				
699	560								
707	715								

From the above table it is seen that for sulphatizing roasting a very careful temperature regulation is necessary. For example, if we take copper sulphate it is seen that at a temperature of 615°C. the dissociation pressure is 70 mm. If the partial pressure in the furnace above the copper sulphate is less than 70 mm., the sulphate will dissociate into CuO and SO_3; if the partial pressure is greater than 70 mm., dissociation will not take place. However, should the temperature of the furnace be raised while the partial pressure of the SO_3 remains constant, the dissociation will be rapid. The gases must, therefore, be removed from the furnace very slowly in order that the partial pressure of the SO_3 be kept above the critical point.

If it is not desired to roast to sulphate but only for the elimination of sulphur, the furnace gases should be removed as rapidly as possible and the temperature of the furnace limited only by the sintering of the ore as this prevents complete roasting of the particles.

Blast roasting is the name given to the process of forcing air through finely divided ignited sulphides, the object being to roast and sinter in a single operation. This type of roasting is a rapid form of roast in which the SO_2 gases are withdrawn very rapidly and the oxidation proceeds with such a speed that the heat generated is sufficient to form a sintered mass of the resulting oxides and the gangue or flux in the ore. A careful temperature control is necessary for if too much heat is generated the charge fuses before roasting has progressed to the desired degree, while if the temperature is too low the resulting product is not properly sintered. Excess heat is taken care of by the following methods:

(*a*) Wetting the charge.

(*b*) Preliminary or rough roasting to reduce the amount of available sulphur.

(*c*) Diluting the ore mixture with inactive fluxes thus reducing the calorific power of the mixture. This method is particularly beneficial in that it keeps the mixture open and permits of a faster roast.

Roasting Arsenides and Antimonides.—When these materials are roasted with free access of air at a low temperature, a part of the arsenic or antimony is oxidized to As_2O_3 or Sb_2O_3 which is readily volatile. Further oxidation changes

these oxides into As_2O_5 or Sb_2O_5 which combine with metallic oxides to form very stable arsenates and antimonates. However, if sulphides are present the sulphur vapor and SO_2 gas reduce the arsenates and antimonates to the sulphide and to the lower oxides which are readily volatile. In general arsenic and antimony are most readily removed by alternate oxidation and reduction.

The reducing roast is used to effect a deoxidation below the fusion point, the material being heated in contact with carbon, sulphur, or reducing gases. An example of the reduction of metallic oxides is the heating of hematite, Fe_2O_3, with coal to form the magnetic oxide Fe_3O_4.

$$3Fe_2O_3 + C = 2Fe_3O_4 + CO$$

The chloridizing roast is used to convert the metals into chlorides preparatory to treatment with solvents. The usual source of chlorine is common salt and it is essential to the success of the process to have sulphides present. A very careful temperature regulation is necessary.

The objects of chloridizing roasting are (Greenwalt, "Hydrometallurgy of Copper"):

1. In copper ores, or in gold or silver ores containing copper, to convert the copper into chlorides which are directly soluble in water or in chloride solutions.

2. In silver ores, or in gold and copper ores containing silver, to convert insoluble metallic silver or its insoluble compounds into the more soluble silver chloride.

3. In any ore, to convert the harmful elements into less harmful compounds.

4. To assist in a more efficient oxidizing action than is possible under the same conditions in ordinary oxidizing roasting.

Ottakar Hofman[1] classified the adaptability of various ores to chloridizing roasting as follows:

1. Those like iron and copper pyrites, gray copper ore, and silver copper glance which in roasting form sulphates and decompose salt, liberating chlorine.

2. Those like galena and blende, which form sulphates remaining indifferent to salt.

3. Antimonial and arsenical silver minerals, which form antimonates and arsenates of silver.

4. The gangue remains indifferent like quartz or porphry, or it takes an active part like limestone, talc, spar, manganese, or minerals containing magnesia.

If the ore consists of minerals of the first group together with an indifferent gangue, chloridizing roasting offers no difficulty and a high chloridization can be obtained without much loss of silver by volatilization and no special skill is required in the roasting; neither does it matter if the salt is added to the charge before entering the furnace or after it has been subjected to a partial oxidizing roasting.

If one or both of the minerals of the second class are present in any quantity the process of chloridizing roasting becomes more difficult. In such a case the time of addition of the salt is very important. If added before the charge enters the furnace a very inferior chloridization is obtained, as is also the case if the salt is added before the oxidizing period has sufficiently advanced.

If all of the above classes of ore are represented the roasting is still more difficult, particularly with a gangue like limestone which takes an active and injurious part in the operation.

Chemistry of Chloridizing Roasting.—The sulphides of iron and copper are mostly relied upon for chloridization. The sulphates formed during the roasting react with the salt to form sodium sulphate and the chlorides of the metals.

[1] "The Mineral Industry," 1896

At the same time some hydrochloric acid and chlorine may be formed due to the action of sulphur trioxide and sulphuric acid:

$$2NaCl + FeSO_4 = Na_2SO_4 + FeCl_2$$
$$2NaCl + CuSO_4 = Na_2SO_4 + CuCl_2$$
$$2NaCl + 2SO_3 = Na_2SO_4 + 2Cl + SO_2$$
$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

The chlorides and chlorine thus formed react with the silver and silver sulphates to form silver chloride:

$$FeCl_2 + AgSO_4 = 2AgCl + FeSO_4$$
$$CuCl_2 + AgSO_4 = 2AgCl + CuSO_4$$
$$2NaCl + AgSO_4 = 2AgCl + Na_2SO_4$$
$$2HCl + 2Ag + O = 2AgCl + H_2O$$
$$Ag + Cl = AgCl$$

Arsenic and antimony form chlorides which are easily volatile. If the ore contains arsenic and antimony in large amounts, much of the silver may be converted in the early stages of the roast into arsenates and antimonates.

Blende, zinc sulphide, in the presence of salt remains indifferent and does not decompose the salt. Zinc sulphate is not decomposed. Zinc oxide may be converted at a red heat into the chloride, which is very volatile.

Galena is converted into lead sulphate which does not react with the salt, and lead oxide which may be converted into the chloride. Both lead oxide and chloride are volatile.

Limestone has a deleterious effect as when roasted with the metallic sulphides it changes in part to calcium sulphate and in part to calcium oxide. Should the ore contain limestone in excess, the sulphides of iron and copper which are needed to decompose the salt will be converted directly to the oxides and a low degree of chloridization will result.

Percentage of Salt.—Ordinarily the amount of salt for silver ores will vary between 1 and 5 per cent, but it is largely proportional to the amount of lime or magnesia in the ore. Copper ores require a larger precentage of salt, 5 to 10 per cent being a fair average for an ore containing several per cent of copper. As the copper content increases the percentage of salt must be increased proportionally. The time of adding the salt depends upon the composition of the ore. An ore low in sulphur may have salt added before charging into the furnace, preferably before the ore is crushed so as to get an intimate mixture. If the ore contains considerable sulphur combined with iron and copper, it may be given a good oxidizing roast before adding the salt and still have enough sulphur to chloridize the silver. If copper is to be chloridized the ore should contain at least as much sulphur as copper before the salt is added. Should the ore be thoroughly oxidized so that it does not contain sufficient sulphur, salt and pyrites may be added. If the salt is added while there is a large excess of sulphur remaining in the ore, it will be largely volatilized, but if added at the proper time the chloridization takes place very rapidly.

Temperature is the all-important factor in chloridizing roasting. Any ore chloridized at an excessive heat will volatilize much of the metals, but if the temperature be kept at the lowest possible point at which the metals can be

chloridized, the time of roasting and amount of air are more or less immaterial.[1]

Roasting Apparatus.—The various types of apparatus used in roasting may be roughly classified as follows:

1. Heaps
2. Stalls
3. Shaft Furnaces
4. Muffle Furnaces
5. Reverberatory Furnaces
6. Cylindrical furnaces with superimposed hearths
7. Blast-roasting apparatus

Roasting in Heaps.—This method of roasting, formerly of common occurrence, has lost much of its former importance, It can be used only for coarse ores, and where the ore is suitable for pyritic or partial pyritic smelting heap roasting is being abandoned. The operation consists in piling the ore in the form of a truncated pyramid on a bed of wood which serves to start the roast. If the ore contains sufficient sulphur to maintain combustion, the roast will proceed of its own accord, a shortage of sulphur will necessitate the admixture of extraneous fuel.

The roast yard must be so situated that the heap is protected from strong winds and so that the prevailing winds carry the sulphurous fumes away from the works. Proper drainage is of importance as the ore after roasting is in a condition to facilitate leaching, and heavy metal losses may occur through this source [2]

The ore is crushed to about 2-in. size and the resulting fines screened out. A layer of fines 4 to 6 in. in depth is spread on the ground and covered with a layer of cordwood, which is arranged so as to form a series of flues leading to chimneys in the central portions of the heap, the chimneys being constructed of boards of sufficient length to reach above the finished heap. The area of the heap is a matter of convenience, the important dimension being the height which varies with the percentage of sulphur in the ore. An ore carrying 15 per cent of sulphur can have a height of 8 ft. above the bed of wood, while one with 35 per cent of sulphur cannot be over 5 ft. The average height of heaps is about 6 ft.

After the cordwood has been placed the coarse ore is piled thereon, and the top and sides of the pile covered with a layer of a somewhat finer ore. After igniting the wood the heap is carefully watched and as the ore becomes ignited and the roast makes progress, a thin layer of fines is spread on the sides and the top of the heap. Should the temperature at any time become too high, the thickness of the layer of fines is increased, while if too cool, some of the fines are removed. The flow of air for the oxidation is regulated at the base of the heap by the addition or removal of the layer of fines at that point. The time required for heap roasting is considerable, 60 to 70 days being required for a heap containing 250 to 300 tons. Upon the completion of the roast the heap is stripped of its covering of fines and the thoroughly roasted coarse ore sent to the blast furnaces, while any partially roasted or fused ore is sent to another heap for further treatment.

The advantages of heap roasting are cheapness of plant and low cost of the roast. The disadvantages are the length of time required, loss of metal by leaching, and, most serious, the killing of the vegetation of the surrounding region.

[1] This forms the basis of such processes as the Swinburne-Ashcroft and Pohle-Croasdale for the recovery of all the commercial metals by volatilizing as chlorides

[2] Or advantage may be taken of this fact for recovering metal as formerly done at some of the Spanish mines.

Roasting in Stalls.—This is an improved modification of heap roasting in which the heap is enclosed on three sides by permanent brick walls, the fourth being added when the roast starts and being removed to facilitate tearing down the heap at the completion of the roast. The chimneys and flues are also permanent and the utilization of heat is more efficient while the draft and collection of the gases are under better control.

Roasting in Shaft Furnaces.—In this type of furnace, which is generally used for coarse ores only, the roast is continuous, the ore and fuel being charged at the top of the furnace and the roasted product withdrawn at the bottom. The amount of fuel required may vary from nothing with rich sulphide ores to 10 per cent with low sulphur ores. The air for the oxidation is furnished by the natural draft of the furnace. The height of the furnace depends upon the size and character of the ore to be roasted; if the material is to move rapidly through the furnace the latter is tapered toward the throat, while if it is desired to have the ore exposed for a considerable time to oxidizing influences the furnace is tapered toward the bottom. When ores are roasted in shaft furnaces and it is not desired to have the ore and fuel in intimate contact, a separate firebox is used. This type of furnace may be used for roasting fine ores by allowing the fine material to slide over inclined shelves retarding its progress sufficiently to effect the desired amount of oxidation. When used in this manner, however, a large amount of dust is produced.[1]

Roasting in Muffle Furnaces.—This type of furnace is used where it is essential that the products of combustion of the fuel be kept separate from the ore. The ores treated are usually fine, and are unsuitable if they are of such a nature that they become sticky during the roast. The air for roasting can be carefully regulated and the composition of the resulting gases kept under careful control and any volatile metals readily condensed and recovered. As the heat from the fuel has to pass through the walls and bottom of the muffle, the fuel cost is high and the progress of the roast slow. The chief commercial application is to blende.

Roasting in Reverberatory Furnaces.—The reverberatory furnace treats fine ores, and the heat for the operation is furnished by burning fuel in a separate compartment, the hot gaseous products passing over the ore which is spread in a thin layer on the hearth, the depth varying with the character of the ore and the ease of roasting. The air for the oxidation may be supplied as excess air in the products of combustion of the fuel, or, more generally, be admitted through the working doors. The ore is fed to the furnace at the cold end and is gradually worked toward the fire end, being stirred at longer or shorter intervals depending on the character of the ore and the thoroughness of the roast desired. The stirring may be done by hand or by mechanical means. The former is expensive and only applicable to small units and is rapidly being replaced by mechanical stirring.

The ratio of the hearth area to the grate area depends upon the nature of the ore; one requiring little heat for oxidation would be treated in a furnace having a high ratio of hearth to grate area and *vice versa*. The height of the roof above the hearth depends to a great extent upon the character of the ore. For fuel economy the lower the roof the more intimate is the contact between the ore and the hot gases. With

[1] If for no other reason than its use for the production of quick lime, and calcined magnesite and dolomite, shaft roasting is of great importance commercially.

ores low in sulphur and a highly oxidizing atmosphere, the height of the roof is dependent upon convenience in stirring the ore. On the other hand, should the ore be high in sulphur, the sulphur dioxide formed must be speedily removed in order to maintain the proper oxidizing atmosphere, and this necessitates the roof being sufficiently high to permit of large volumes of air passing over the hearth.[3]

The process may be intermittent or continuous. Where small quantities of ore are to be treated or the installation of an expensive furnace is not warranted, a small hand-worked furnace would be used. Those are cheap in construction but expensive to operate. The furnace is charged with the ore which is rabbled by hand until the roast is complete when it is withdrawn from the furnace and a new charge introduced. Should there be a considerable supply of ore, the process would be made continuous by lengthening the hearth to a greater or less degree depending upon the time the ore has to remain in the furnace. If the ore is to be hand stirred the width of the furnace is controlled by the ability of the workman to reach and stir the ore with convenience, a furnace worked on one side only being limited to a hearth width of about 8 ft. while if worked from both sides the width may be 14 to 16 ft. For hand work the working doors must be spaced sufficiently close to permit of easy rabbling, and if they are spaced too far apart, the ore in the intermediate spaces will seldom be stirred.

Hand worked reverberatories are rapidly being replaced by the more efficient mechanically worked furnaces, due to the high cost of labor, which is the chief item of expense, and also due to the fact that the quality of the labor is variable and has a great effect on the quality of the roasted product. The mechanically worked furnaces are under better control, the operation is more regular, and the output per square foot of hearth area is greater. They have the disadvantage that more dust is produced and difficulty is experienced with ores that become sticky during the roast as this type of ore clogs up the rabble arms and often causes serious difficulties. However, these disadvantages are more than offset by the gains. Some types of mechanically operated reverberatory furnaces are:

Edwards Furnace.—This is a straight-line furnace 76 ft. long by 6 ft. 6 in. in width; the hearth is sloped from the feed end to the discharge end ½ in. to the foot. It is heated by two fireboxes, one at the discharge end, the other being placed about 30 ft. distant. The ore is fed at the cool end from which it is worked down the inclined hearth to the discharge end where it is discharged through an opening in the hearth. The stirring is done by 21 horizontally revolving arms fastened to a vertical water-cooled spindle passing through the roof of the furnace and being driven by bevel gears. Each spindle moves in the direction opposite to the adjacent one, the circle of rotation of the end of the rabble arm overlapping that of the adjacent rabbles, so that the particles of ore move through the furnace in a zig-zag path. In the Duplex type of furnace the width of the hearth is 13 ft. and there are two rows of rabbles. The following table taken from Hofman's "Metallurgy of Copper" shows the work of the Edwards furnace at the Yampa plant when roasting copper ores:

	Simplex	Duplex
Hearth, feet	6 × 57	11 × 92
Inclination of hearth, inches per foot	½	⅝
Spindles, revolutions per minute	2	1
Power, horsepower	1	4
Capacity in 24 hr., tons	25	72
Sulphur in raw ore, per cent	26–39	
Sulphur in roasted ore, per cent	2.2–8.6	
SO_2 in flue gases, per cent	4.3	

Merton Furnace.—This is a multiple-hearth furnace having three superimposed hearths. The ore is fed at the cool end of the upper hearth and moved by revolving rabble arms in a manner similar to the Edwards furnace. Upon reaching the end of the first hearth the ore falls through a drop hole to the second hearth and similarly to the third hearth from which it passes to a finishing hearth having a water-cooled spindle and rabble arm. The roasting hearth is 24 ft. long and 8 ft. wide and each hearth has four rabble arms. The power required is 2 hp. and the capacity per 24 hr. is claimed to be as follows: Sulpho-tellurides 18 to 25 tons; pyrites 6 to 15 tons; sulphide copper ores 10 tons; galena 8 to 20 tons.

The Ropp furnace is a straight-line single-hearth furnace with an area of 150 by by 14 ft. and has four fireplaces. Through the center of the hearth there is a slot through which passes a heavy steel plate to which is attached a rake extending the width of the hearth and having teeth set at an angle of 45 deg. The steel plate supporting the rake is attached to a small truck which is moved along a track by a steel cable. The rakes move slowly through the furnace from the feed end to the discharge end, continually stirring the ore, and at the discharge end return to the feed end alongside the furnace during which time they are thoroughly cooled by the air. Each truck makes a complete circuit in about 5 min. The furnace requires about 5 hp. and will roast 50 to 75 tons of sulphide ores per 24 hr.

The operation of the Wethey furnace is similar to the above except that the trucks supporting the rake carriers move on tracks outside the furnace and return to the feed end over the top instead of along the side. The Wethey multiple-hearth furnace is a double furnace with four superimposed hearths having drop holes alternately at opposite ends so that the ore may pass from one hearth to the next. The single-hearth type with 1,000 sq. ft. of hearth area will handle 70 tons per 24 hr. and requires 15 hp.

The Pearce turret furnace has an annular hearth open at one point to permit ore being fed and discharged. It is made with one or two hearths, but as many as six hearths have been tried. The furnace is heated from three exterior fireplaces and the ore is stirred by two air-cooled rabble arms passing through a slot in the furnace wall, the slot being kept closed by a steel band which moves with the rabble arms. The mechanism for operating the rabble arms is located on the inside of the annular ring. The teeth of the rabble arms are so arranged that the ore on the outer edge of the hearth, which has the greater distance to travel maintains its relative position to the ore on the inner edge. A single-hearth furnace having an area of 505 sq. ft. will handle 14 tons of copper sulphide concentrates per 24 hr.; a double-hearth furnace with an area of 1,010 sq. ft. will treat twice this amount.

The Brückner Furnace.—At one time this was an extremely popular furnace but due to its small capacity it is fast being discarded by the larger plants. It is composed of a brick-lined horizontal cylinder with truncated ends, revolving on two friction rollers between a firebox at one end and a flue at the other. The firebox runs on tracks so that when roasting high sulphur ores one firebox can serve several furnaces. There are four discharge openings in the horizontal portion of the cylinder. The furnace requires 2 hp. and makes eight revolutions per hour. Working on Butte concentrates it will rough roast 15 tons per 24 hr. The operation requires 2 hr. time in drying the ore, 4 hr. in bringing it to the roasting temperature, and the remaining 18 hr. in completing the roast and discharging the roasted product. Due to the furnace having such small dimensions (16 ft. long by 8 ft. in diameter) the fuel consumption is high, and the stirring of the ore by the rotation of the cylinder causes a very heavy production of dust.

The cement kiln is at present being used to some extent for the roasting and sintering of flue dust, fine concentrate, etc. The kiln may be fired with powdered coal or oil, and the size of the sintered product depends upon the amount of fuel used per

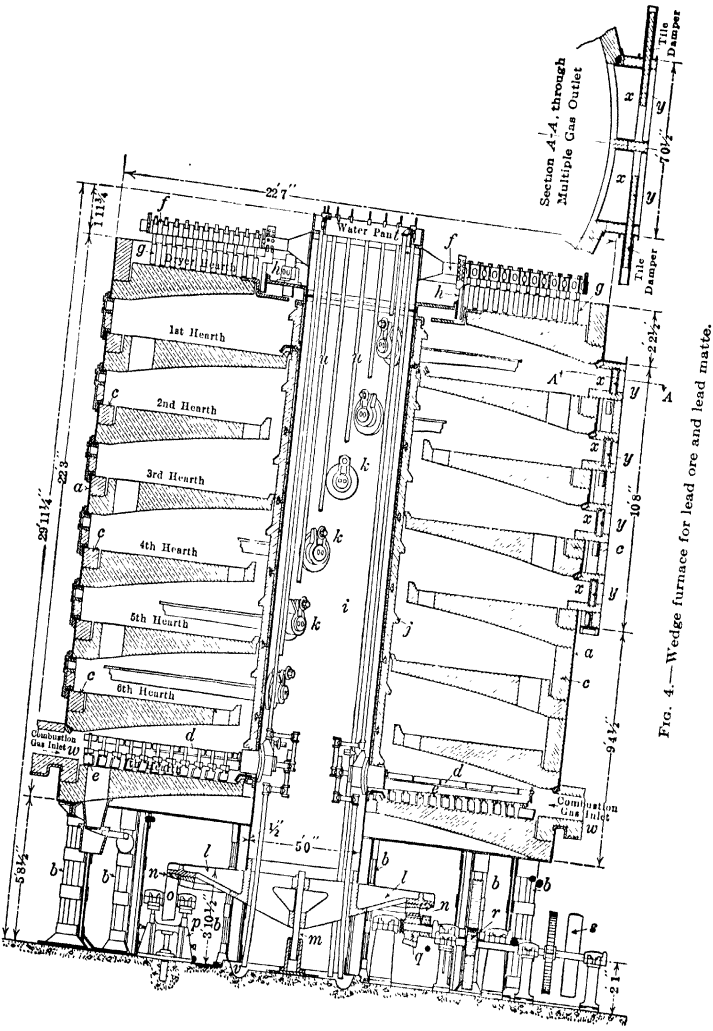


FIG. 4.—Wedge furnace for lead ore and lead matte.

ton of material. A 60-ft. kiln will treat 50 to 75 tons of material per day depending upon its nature.

Cylindrical Furnaces with Superimposed Hearths.—This type of furnace is rapidly becoming universal for the roasting of fine material. It consists of vertical brick-lined iron or steel cylinders having, in some cases, as many as seven superimposed hearths. When used for the roasting of material high in sulphur, sufficient heat is generated to carry on the roast without the use of extraneous fuel. When used for dead roasting, sulphatizing roasting, or chloridizing roasting a firebox is used and can be so arranged that the hot gases enter the lowest hearth or any or all of the upper hearths. There is a central rotating shaft which carries radial stirring arms having blades set at the proper angle for stirring and moving the material. The ore is fed to the top hearth where it is stirred and moved by the rabbles from the periphery to a drop hole in the center where it falls to the next hearth on which it is

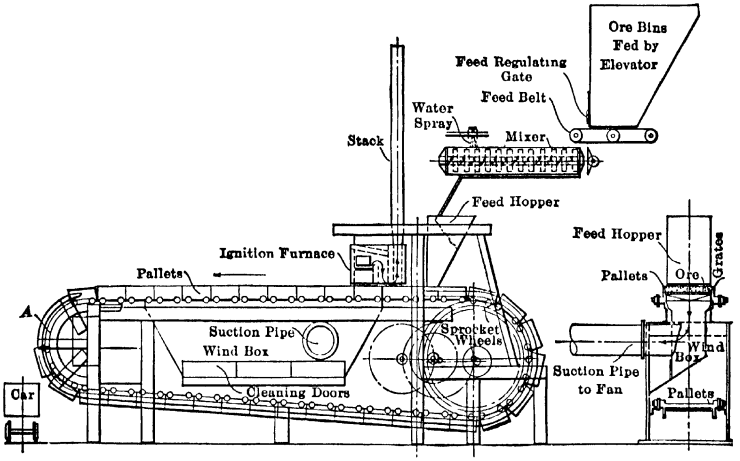


FIG. 7.—Dwight-Lloyd straight-line machine.

moved from the center to the periphery, and so on until it is discharged from the lowest hearth. The necessary air for the roasting is supplied through the working doors and travels in a direction opposite to the movement of the ore. The leading types of this furnace are the Herreshoff, Wedge, and Evans-Klepetko. The capacity of this type of furnace depends largely upon the size and the character of the material treated, and varies from 20 to 80 lb. per square foot per 24 hr.

Blast-roasting Apparatus.—Blast roasting is conducted in both up-draft and down-draft apparatus; the latter appears to be gradually replacing the former. Typical examples of the two methods are the Huntington-Heberlein pots for up-draft work, and the Dwight-Lloyd straight-line machine for down-draft roasting.

The Huntington-Heberlein pots are made of cast iron and are about 9 ft. in diameter with a depth of about 4½ ft. and will hold 8 to 10 tons of ore. Owing to the severe strains undergone during the operation the pots are usually cast in flanged sections of four sides and a bottom which are bolted together. About 18 in. above

the bottom is a circular cast-iron grate 6 ft. in diameter which is perforated with numerous ¾-in. holes and which serves to distribute the blast which enters the pot beneath the grate through a blast pipe 5 to 6 in. in diameter. During the blowing the pot is covered with a movable hood connected with a flue which carries off the waste gases. The method of operating the pots is to spread a layer of hot coals on the grate and start a light blast. About 2 tons of ore is charged on the hot coals and as the roast gains headway, the balance of the charge is added and the blast pressure gradually increased to its maximum of about 12 oz. The blow is complete in from 8 to 10 hr. after which the blast is turned off and the pot emptied by means of a crane. The cake is then broken up and sent to the blast furnaces.

The Dwight-Lloyd straight-line sintering machine consists of a structural steel frame which supports a feed hopper, an ignition furnace, a suction box, and a pair of endless tracks or guides upon which move a train of grates on wheels, known as pallets, forming a continuous conveyor. At the discharge end of the machine the guides curve downward and pass under the machine back to the feed end. At this point there is a break in the continuity of the train of pallets in order to facilitate the discharge of the sintered material. The suction box is connected with an exhaust fan maintaining a vacuum of 5 to 10 in. of water and the top is accurately machined so that when the pallets pass over they can slide over this smooth surface making a contact that is as airtight as possible. The pallets are moved by sprocket wheels which lift them from the guides underneath the machine to the upper guides and push them under the feed hopper. As each pallet is pushed by the one behind it, the joints are kept closed and the air leakage reduced to a minimum. The speed of travel varies from 18 to 36 in. per minute. The ignition furnace, which may be fired with coal, gas, or oil, is placed across the line of pallets and is so arranged that the flame is deflected downwards upon the layer of ore carried by the pallets. As the roasting occurs only when the ore is over the suction box, the area of the latter is the effective hearth area of the machine.

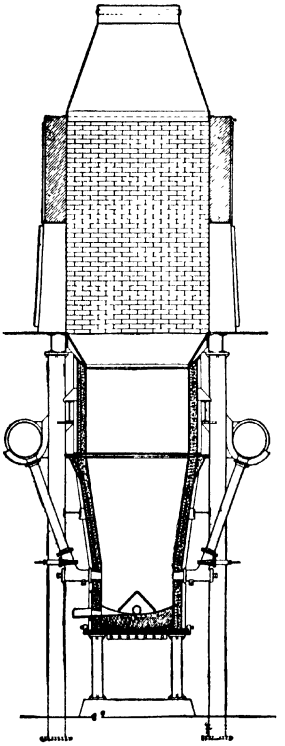
The operation of the machine is as follows: The ore and flux are conveyed to a receiving hopper having a gate to regulate the discharge to an endless belt which conveys the material to a horizontal mixer where the ingredients are thoroughly mixed and any necessary amount of water added, the mixer discharging to the feed hopper of the machine. As the pallets are pushed by the sprocket wheels to their position under the feed hopper, they receive an even layer of ore about 4 in. in thickness and then pass under the ignition furnace where the top surface of the ore is ignited. At the same time the pallet engaged the suction box and the downward flow of air causes the ignition and sintering to progress from the surface toward the grates. The speed of the pallets is so adjusted that as a pallet leaves the suction box the sinter is complete. The pallets now move towards the discharge end and, if too hot, are sprayed with water to reduce the temperature. On reaching the discharge point, where there is a break in the continuity of the train of pallets, the pallet drops into the guides leading beneath the machine and at the same time strikes the pallet which has immediately preceded it, with sufficient force to dislodge its load of sinter which is discharged into a chute leading to a hopper or car. The pallets now return, by gravity, beneath the machine to the sprocket wheels. The machine has a capacity of from 50 to 200 tons per 24 hr. depending upon the nature of the material being treated.

A continuously rotating wheel on which the charge was spread was formerly used in the same way, the charge being ignited by a fire box occupying part of the periphery (if the axis was horizontal) or a sector of the circle (if it was a horizontal circular surface revolving about a vertical axis), the suction box coming next, then a cooling portion, and finally the material being scraped off.

THE SMELTING OF COPPER ORES

By F. R. Pyne[1]

The World's Copper Supply.—The great bulk of the world's production of metallic copper is derived from sulphide ores. Oxide ores, which occur to a small extent, are usually mixed with sulphides for smelting, or are subjected to hydrometallurgical treatment. Native copper ores, such as occur in the Michigan peninsula, consisting as they do of particles of metallic copper disseminated throughout the accompanying gangue, require simply a fusion (usually preceded by concentration) with sufficient flux properly to slag the gangue, but such ores are entirely insufficient to supply the world's consumption.



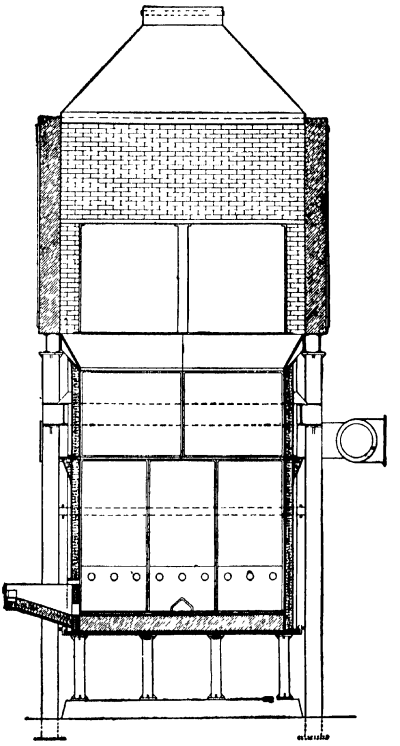


Fig. 5.—Standard matting furnace—vertical section.
Fig. 6.—Standard matting furnace—vertical section.

The sulphide ores of copper may be considered as mixtures of copper and iron sulphides accompanied by siliceous or basic gangue and the object of smelting is to cause by fusion the conversion of the gangue into a valueless slag by the addition of proper fluxes, and at the same time to concentrate the copper and other valuable constituents of the ore, such as silver and gold, into a small amount of high-grade material, this high-grade material then being submitted to oxidation to eliminate all but the valuable portions which it is desired to recover. In order to accomplish this

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result advantage is taken of the strong affinity of copper for sulphur and its weak affinity for oxygen in comparison with iron and the other base metals in the ore.

Slag and Matte Formation.—There are two important materials formed during the smelting of copper-sulphide ores; the slag produced by the combinations of the gangue of the ore and the flux, and the matte which is the product of the fusion of the metallic sulphides: of these two products, the slag receives the first consideration of the metallurgist, as the sulphides melt readily under almost any circumstances while unless the slag-forming constituents are properly proportioned, serious difficulties will result. A satisfactory slag must possess the following qualifications:

1. It must be as economical as possible and to this end the other qualifications are subordinated, as a scientifically perfect slag may in the end be so expensive that any margin of profit is wiped out by its cost.

2. It must be sufficiently liquid to flow freely, but should not require such a temperature that an excessive amount of coke is necessary to produce it.

3. The specific gravity should be sufficiently below that of the matte to permit the latter to separate from it thoroughly.

The following slags are illustrative of general copper practice:

	Per cent					
	1	2	3	4	5	6
SiO_2	32 5	34 0	44 5	39 3	42 2	42 0
FeO	52 2	46 0	39 7	21 8	39 4	22 0
CaO	4 8	11 0	9 9	25 2	7 0	26 0
Al_2O_3	7 2	5 0	6 2	6 2	4 0	4 0
Cu	0 39	0 69	0 21	0 3	0 29	0 23

Matte is the product of fusion of metallic sulphides. Upon fusion of a mixture of copper-iron sulphides, a certain part of the sulphur is volatilized while of the remainder sufficient is seized by the copper to form cuprous sulphide, Cu_2S, the balance being taken up by iron and other base metals in the order of their affinities to form sulphides.

For all practical purposes, copper matte may be considered to be a mixture of Cu_2S and FeS in varying proportions. Matte is also an excellent collector or gold, silver, and other precious metals.

The amount of matte produced in smelting is dependent upon the sulphur in the ore. An ore high in sulphur and iron but low in copper will, upon fusion, produce a matte containing so low a percentage of copper that its treatment would, under ordinary circumstances, cost too much, and as it is the desire of the metallurgist to concentrate the copper in his ores up to the most economical point, steps mustbe taken to reduce the amount of sulphur available for the formation of matte and lower the amount of the latter produced per ton of ore smelted.

Such reduction in the sulphur content may be accomplished in two ways; by subjecting the ore to an oxidizing roasting or by subjecting it to an oxidizing fusion. The latter is used where the ore occurs as massive sulphides and will be considered later under "Pyritic Smelting." If the ores are not massive sulphides, oxidizing roasting is the predominating method. In roasting the object is to oxidize the excess

sulphur to SO_2, at the same time oxidizing the excess iron which will then be available for use as flux for the silica in the ore and thereby save an equivalent amount of expensive foreign flux. An ore low in copper will require a greater amount of roasting than one rich in copper in order to produce a matte with the desired copper content.

The following table is illustrative of mattes[1] formed in copper smelting:

	Per cent					
	1	2	3	4	5	6
Cu	49 2	55 0	54.9	60 7	48 2	44 6
S	19.5	24 0	23.4	23 3	23 7	23 5
Fe	22.8	13 9	20.3	11.4	24.7	27 0

There are two kinds of apparatus in which the smelting is conducted; the blast furnace and the reverberatory furnace. The blast furnace is used for the treatment of coarse ores and the ore and fuel are in intimate contact, the fuel being burned by a blast of air forced through the body of the charge. The reverberatory furnace is used for the treatment of fine ores and the fuel and ore are kept separate, the former being burned in a separate compartment from which the flame and hot gases pass over the ore being guided by a more or less horizontal roof. The heating of the ore is accomplished by the radiation from the roof and walls rather than by contact with the hot gases.

The modern copper blast furnace consists of a water jacketed shaft having an oblong cross-section and varying in height from 15 to 20 ft. The water jackets throughout the shaft are necessitated by the furnace running with a hot top due to the large amount of air forced through the charge and also by the low charge column, both of which are an aid to the obtaining of a pyritic effect so much desired by copper metallurgists. The oblong cross-section of the shaft is due to the fact that the width at the tuyere level is limited by the ability of the blast to penetrate the charge. This dimension varies from 44 to 56 in. and this being fixed, the only manner in which an increased capacity is obtained is by lengthening out the furnace and modern furnaces have lengths varying from 180 in. to as much as 1,044 in. in the case of the huge furnaces at Anaconda. The ends of the furnace are generally vertical while the sides are boshed or sloping. The amount of bosh for the sides is governed by the amount of reducing action to which it is desired to subject the charge; the greater the bosh, the stronger will be the reducing action. In furnaces where there are two tiers of water jackets, the usual practice is to have only the lower tier of jackets boshed, the upper tier being vertical. The amount of bosh per foot of height varies from 1 to 2 in.

The blast enters the furnace through tuyeres passing through the water jackets. The pressure varies with the width of the furnace, the number of tuyeres, the amount of fines in the charge and the height of the ore column, a fair average figure being about 36 oz.

The lowest point of the furnace consists of a shallow hearth or crucible in which the molten slag and matte are collected. The crucible may be built up solid from the

[1] In general mattes carry about 23 per cent of sulphur, a fact, I believe, first pointed out by Dr. Edward Keller, and in any calculations concerning matte-smelting this figure is a safe one to use in calculating the charge, correcting the charge later by actual furnace results.

foundations but the general practice is to build it upon ribbed cast-iron plates supported by jack screws. The refractory lining of the crucible is generally made of a good grade of fireclay brick though special circumstances may require the use of silica or chrome brick. The outside of the crucible is encased in heavy cast-iron plates bolted securely together, these plates also serving as a support for the lower tier of water jackets.

The upper part of the furnace consists of a brick or metal flue through which the waste gases are led off into a dust chamber. Feed openings located just above the upper tier of water jackets and occupying the entire length of the furnace, are used, the charges of fuel and ore being shoveled through by hand or else dumped from a car. Between charges the feed openings are kept closed by sliding doors.

The slag and matte are continuously discharged from the crucible through a water cooled breast jacket into a spout, which conveys the mixture to a forehearth or settler.[1] The overflow end of the spout is higher than the opening in the breast jacket so that when the spout is filled with molten material the blast is trapped. The spout is usually constructed of water-cooled iron, copper, or bronze, though the presence of a highly corrosive matte may necessitate the use of chrome or magnesite brick.

The settler serves not only as a means of separating the matte and slag by reason of the differences in their specific gravities but also as a reservoir for the accumulation of matte until such time as it is required. A plant which treats its own matte, therefore, requires a larger settler than does one which casts its matte direct into molds for shipment to some other plant for treatment. The settler is circular or oval and consists of an iron shell lined with refractory material. There are usually two matte taps, located in the lower part of the settler, which are kept closed between taps by clay plugs. The slag overflows from the top of the settler into a pot car or else into a launder where it is granulated by water.

The following table gives data concerning some modern copper blast furnaces.

	Tenn. C. & C. Co.	Granby	Anaconda		Garfield
Section at throat	72 by 270	64½ by 266½	72 by 612	72 by 1,044	66 by 240
Section at tuyeres	56 by 270	44 by 266½	56 by 612	56 by 1,044	42 by 240
Height, tuyeres to throat	18 ft. 3 in.	12 ft. 10 in.	13 ft. 10 in.	13 ft. 4 in.	13 ft.
Number of tuyeres	25	30	88	150	44
Diameter of tuyeres	4½ in.	5 in.	4 in.	4 in.	4 in.
Tons per 24 hr	441	515	1,460	2,500	560 to 750
Tons per square foot hearth area per 24 hr	4.30	6.32	5.88	6 17	8.00 to 10.71
Blast pressure, ounces	45	26.30	40	40	38 to 41

[1] There are a few small old-fashioned furnaces in which the slag and matte are tapped intermittently. These are known as "internal settlers" The slag tap is on a higher level than the matte tap With these furnaces the slag may be run continuously or almost so, and the matte only tapped intermittently.

Sub-divisions of Blast-furnace Smelting.—In blast furnace smelting there are three distinct processes:

1. The reduction process in which a considerable percentage, 12 to 15, of coke is used. The blast oxidizes the carbon of the coke but not the sulphur of the ore. This process is the one most generally used.

2. The pyritic process in which raw massive sulphides are smelted in a highly oxidizing atmosphere without the addition of carbonaceous fuel. The heat generated by the oxidation of the sulphur and iron is sufficient to maintain a continuous operation.

3. The partial (or semi-) pyritic process in which sufficient heat is not generated by the oxidization of the sulphide ores and carbonaceous fuel is added to the charge in barely sufficient quantity to overcome the deficiency.

The Reduction Process.—This process is characterized by the use of carbonaceous fuel as the principal source of heat. The sulphur content of the charge is sufficient to form the desired matte and any oxidation is generally undesirable. The percentage of coke, which is the chief carbonaceous fuel, varies from 12 to 15 per cent. An excessive amount of coke is likely to cause a reduction of iron from the slag, while with a shortage the furnace becomes chilled and suffers a loss of tonnage.

The use of such an amount of coke means that the furnace always contains a large mass of glowing coke for a considerable distance above the tuyeres and consequently the oxygen of the blast is consumed almost immediately resulting in a strong reducing atmosphere. Such being the case, it is readily seen that any sulphides present will melt down unchanged and form matte. An ore high in sulphur would, therefore, yield a large amount of matte which is expensive to treat and it is clear that little would be gained by the reducing smelting of such an ore and that a portion of the sulphur must be eliminated by roasting previous to the treatment in the blast furnace, or the sulphides may be mixed with oxide copper ores to increase the grade of the matte. A certain oxidation of sulphur may be accomplished in the blast furnace by keeping the ore column low and increasing the blast but such procedure results in a very hot top and high temperatures of the waste gases and in general is uneconomical.

Regarding the chemistry of the process, the blast entering through the tuyeres oxidizes the carbon of the coke to CO which is partly oxidized to CO_2, the resulting gases being a mixture of CO, CO_2, and the nitrogen of the air.[1] As these gases rise in the furnace and reduce the oxidized materials, the percentage of CO_2 increases and will predominate in the waste gases. Any unchanged CO is usually burned to CO_2 at the top of the ore columns. As the ore charge descends in the furnace, its moisture is driven off almost immediately, followed by the decomposition of such carbonates as may be present. At a lower point the oxides and silicates of copper will be reduced and on coming into contact with metallic sulphides will be converted to sulphides which, together with any existing copper sulphides, melt and flow downwards to the crucible collecting the silver and gold in the ore as they descend. Ferric oxide, Fe_2O_3, is reduced to the ferrous condition, FeO, and when the temperature becomes sufficiently high, which occurs a short distance above the tuyeres, unites with silica to form slag, as does also any lime or other flux added to the charge.

The molten materials having collected in the crucible below the tuyeres the sulphides adjust themselves to form the proper matte, and likewise the various slag components to form the proper slag.

[1] But in only one or two plants in the world does the proportion of CO become high enough to use the gas as a fuel, as may be done with the gases from iron smelting.—EDITOR.

The Pyritic Process.—The feature of this type of smelting is that the heat necessary to conduct the operation is furnished by the oxidization of the constituents of the ore, no extraneous fuel being used for this purpose. Up to 2 or 3 per cent of coke may be added but its function is probably to preheat the charge and it never reaches the actual smelting zone.[1] The essential requirements for pyritic smelting are siliceous material high in free silica, and heavy pyrite ore. It is necessary for as much of the silica as possible to be in the free state in order that it may combine with the ferrous oxide at the instant of its formation, combined silica is unsuitable for the pyritic process as it is already united with one or more bases and consequently requires a large amount of heat to break up the existing combinations and form new ones with the ferrous oxide. The pyrite ore not only furnishes the heat for the operation but also the matte required and it must largely consist of iron pyrites, as any oxidation of the copper sulphide would result in the slagging and loss of the resulting copper oxide.

The blast entering the furnace through the tuyeres strikes the hot fused sulphides and oxidizes the FeS to FeO and SO_2, the FeO simultaneously uniting with silica to form a ferrous-silicate slag while the SO_2 rises through the charge and preheats it, assisted by the oxidation of such coke as may be present.

$$C + SO_2 = S + CO_2$$

As the charge sinks in the furnace the moisture is driven off quickly followed by the dissociation of the limestone added as flux. When the smelting zone is reached the sulphides fuse and run down over the gangue and flux and are oxidized by the blast as described above. The matte collects below the tuyeres as does also the ferrous silicate slag after uniting with the lime to form the final slag. The slag and matte mixture then flows through the spout to the settler.

The grade of matte produced and the degree of acidity of the slag are controlled by the volume of air blown into the furnace. Any reduction in the air will cause less of the sulphide to be oxidized and the grade of the matte will be lowered, and as less iron is oxidized the slag will become excessively siliceous and interfere with the process unless the amount of siliceous material has been correspondingly reduced. On the other hand, an increase in the amount of air oxidizes additional iron, raising the grade of the matte and increasing the iron in the slag unless additional silica is provided.

A peculiarity of the pyritic process is the artificial bosh formed on the side and end walls of the furnace. This contracts the smelting area to a long narrow slit. The bosh composed of fragments of quartz or gangue rock stuck together by slag or by superficial softening, seldom contains any matte. Its position in the furnace is not fixed but varies under different conditions.

In reducing smelting the tuyeres are bright, in pyritic smelting they are dark and are bridged across. It has been stated that a bar can be passed through the furnace from one tuyere to the opposite tuyere and be cool when withdrawn. This indicates that the zone of fusion is well above the tuyere line and that the molten material passes through channels between the tuyeres.

Partial pyritic smelting is used when the available sulphide ores are not massive but consist of pyritic material disseminated throughout the gangue which is generally low in free silica and usually contains alumina. Such ores are not capable of furnishing by themselves sufficient heat for the continuance of the proc-

[1] It probably also aids by securing a certain looseness of charge —EDITOR.

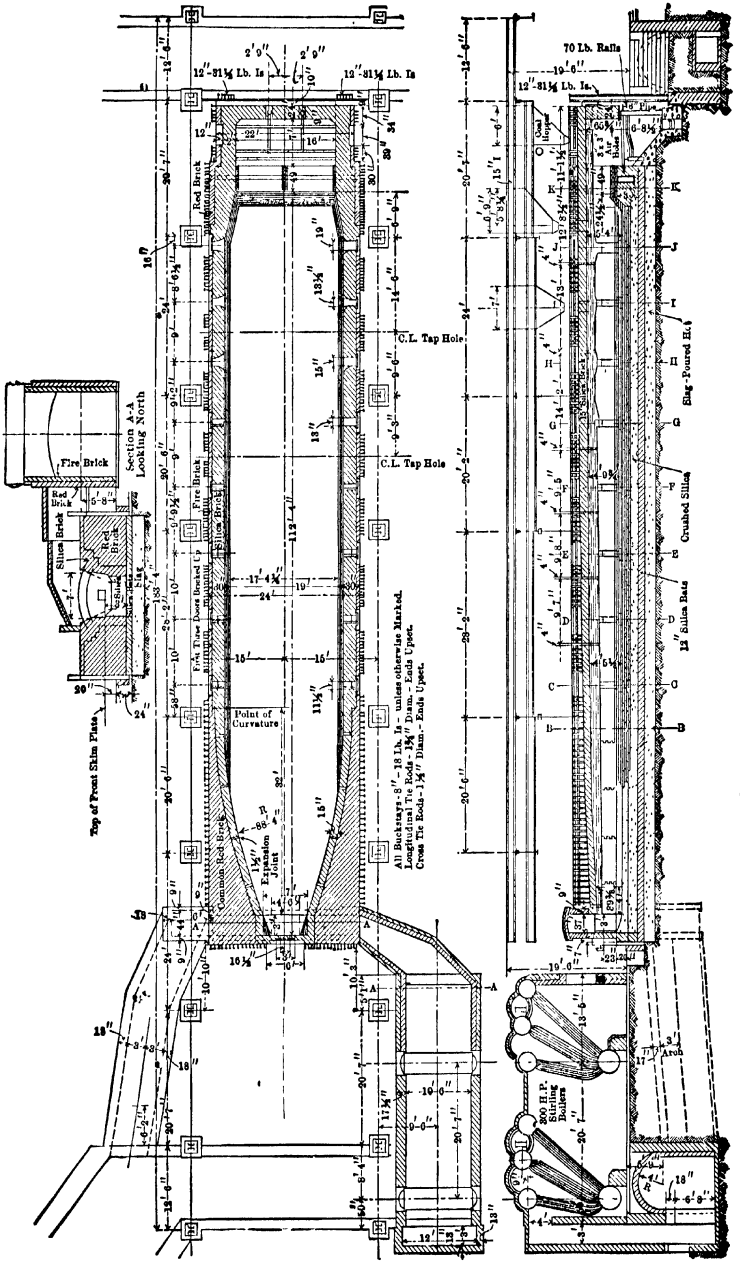


FIG. 9.—Reverberatory for smelting copper ores.

ess and it is, therefore, necessary to add carbonaceous fuel up to about 8 per cent. Preheating the blast has been found advantageous in some instances. In the partial pyritic process the slags are high in silica and lime but low in iron and frequently contain considerable alumina. Due to the presence of carbon a large volume of air is necessary in order that the atmosphere shall be sufficiently oxidizing to obtain any considerable pyritic effect. This results in the furnace having a very hot top. The smelting zone is nearer the tuyere level and is not so contracted as in pyritic smelting, but higher and more contracted than in reducing smelting. The tuyeres are frequently dark and require a great deal of punching to keep them open.

In reverberatory smelting the ore supply is generally fine sulphide ores which have been given a preliminary rough roasting. This is smelted on a hearth with the addition of proper fluxes, to a matte containing 35 to 45 per cent copper, and a slag containing 35 to 40 per cent of silica. The reducing agent is the sulphur remaining in the ore, the fuel used not being in contact with the ore serves only to obtain the desired temperature.

The hearth of the reverberatory furnace is generally made of silica sand sintered into place though silica and magnesite brick have been used. It is long and narrow, the width being limited to about 18 ft. by the difficulty and cost of maintaining the roof. The capacity therefore depends upon the length and this is limited only by the ability to maintain the proper temperature at the flue end. In the most recent furnaces the length is 135 ft. though present practice is to limit it to about 112 ft. The former practice of having a vault under the hearth has been abandoned in favor of a solid bottom in order to economize on heat, as any radiation through the hearth seriously curtails the rate of smelting. The hearth is enclosed in silica- or clay-brick walls which are about 24 in. thick to reduce radiation to a minimum. They are heavily ironed and buckstayed for resisting the thrust of the hearth and its contents. The roof is invariably constructed of silica brick varying in thickness from 15 to 20 in.

Modern reverberatories have no side doors, the charges being introduced through holes in the roof along the side walls, the practice being small charges at frequent intervals. The charge consequently lies against the side walls, protecting them from the hot gases, and as it gradually melts more charge is introduced. A deep bath of matte is carried on the hearth and serves to equalize and distribute the heat, thus preventing the overheating of any part of the hearth with possible damage to the furnace. It also is of great assistance in rapidly heating up the fresh charges as they are dropped into the furnace as the matte being highly superheated readily gives up its heat to the cold charge above it, while the hot furnace gases heat the charge from above. The matte is tapped as desired from the end of the furnace while the slag may flow off continuously or be skimmed periodically; the former method is coming more into favor as it gives a cleaner slag.

The fuel used may be soft coal fired by hand or in stokers, pulverized coal, oil, or producer gas. The largest plants are rapidly changing from hand firing to pulverized coal or oil on account of the more economical handling and the greater thermal efficiency obtained. The ratio of charge to fuel will average about as follows:

Soft coal	4:1
Pulverized coal	7:1
Oil	0.6 to 0.7 bbl. per ton charge.

Flue-dust is an important though undesirable by-product from the roaster, blast furnaces and reverberatories and the recovery and working up of this material is a considerable item in the cost of operation. The recovery may be

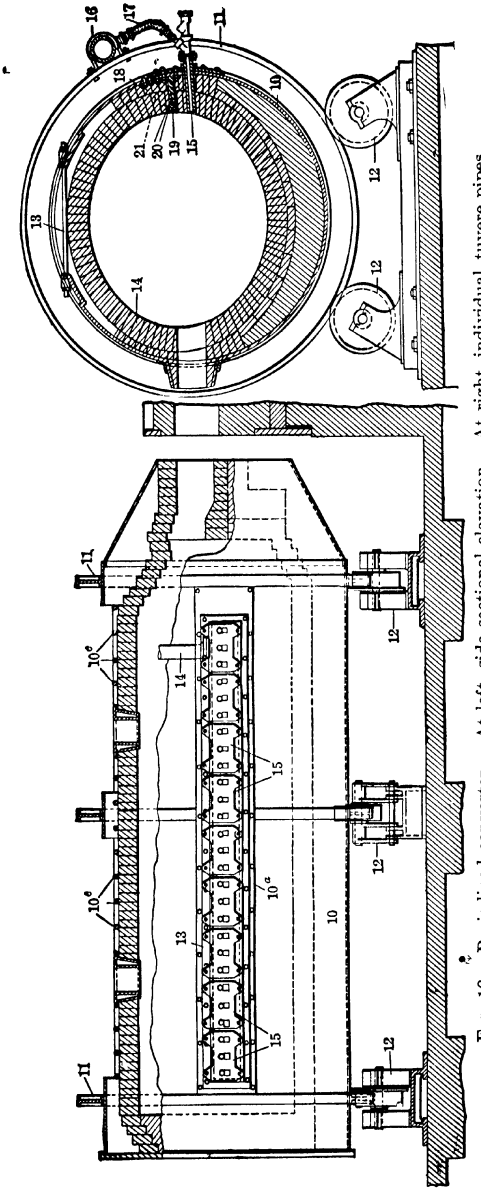


FIG. 10.—Basic-lined converter. At left, side sectional elevation. At right, individual tuyere pipes.

accomplished by one or more of the following methods; passing the gases through large dust chambers in which the velocity is so reduced that all but the very finest particles will settle out; by filtering the gases through woolen bags after previously cooling to a proper temperature; by electrostatic precipitation as in the Cottrell process; or by causing the suspended particles to impinge upon wires or baffles hung in a dust chamber as in the Roesing system. The treatment of recovered flue-dust consists of briquetting and smelting in the blast furnace, a method formerly widely practiced but now rapidly falling into disuse; agglomerating in rotary kilns, Dwight-Lloyd sintering machines or Huntington-Heberlein pots; incorporating with converter slag and smelting in the blast furnace; or by direct smelting in the reverberatory furnaces, the last method being the most satisfactory.

Metal loss is a very important element in smelting costs and one which is watched and studied carefully in order to reduce it to a minimum. The three chief sources are dust loss in handling, losses in slags, and losses in flue dust and fume. The loss in handling increases with the fineness of the ore and may amount to a considerable amount; the loss in slags is the largest source owing to the relatively enormous amount of slag produced though the assay may be low; and the dust and fume loss will depend upon the fineness of the ore, the amount of volatile constituents, and the facilities for recovering the flue-dust.

Comparing blast furnace and reverberatory smelting, the former requires coarse ore in order to work satisfactorily, little space is required and the investment is low for any given tonnage, the fuel though small in amount is relatively expensive, and considerable power and cooling water are required. Blast-furnace slags can be made between widely varying limits but the addition of a large amount of flux causes a large amount of slag with a corresponding metal loss. The reverberatory furnace is the most satisfactory and advantageous apparatus in which to treat fine ores but as it requires an extensive roasting plant and in itself occupies a large amount of space and locks up a large amount of valuable metal, the investment is large for any given tonnage. While large amounts of low-priced fuel are consumed, a large amount of the heat in the waste gases is recoverable in waste heat boilers which greatly reduce the power costs. The amount of slag and consequently the metal loss is less than the blast furnace. With the ever increasing amount of fine ores, the reverberatory is fast displacing the blast furnace and it has been found advantageous in certain localities to use reverberatory smelting for coarse material that under ordinary conditions would go to the blast furnace.

Converting.—The copper and other valuable ingredients of the ore having been concentrated into matte, and the valueless material disposed of as slag, the next step in the process is the removal by oxidation of the iron and the sulphur. This is accomplished by transferring the molten matte to a refractory lined vessel, known as a converter, and forcing thin streams of air through the liquid mass. The iron in the matte is oxidized to FeO and immediately combines with silica to form slag while the sulphur is oxidized to SO_2 and passes off in the waste gases. The copper together with any gold or silver is reduced to the metallic form and is cast into suitable shapes for transportation to the refinery.

The converter is a cylindrical iron or steel vessel lined with refractory material. A conical mouth is provided through which the matte is introduced, the slag and

blister copper withdrawn, and the gases pass to the stack. The air for the oxidation is introduced through the side of the converter by means of tuyeres leading from an air box attached to the outside and having a connection to the high pressure air main.

Converters are classified as upright or horizontal, depending upon the direction of the long axis of the cylinder and are so mounted that they can swing in a vertical plane for the purpose of receiving or withdrawing the molten contents.

The refractory lining is composed of either acid or basic material, the acid lining though formerly universal is rapidly being supplanted by the basic lining. In the acid-lined converter the material used should contain the largest possible amount of free silica consistent with proper mechanical strength. The material generally used is low-grade siliceous ore, for while this may not be so desirable metallurgically as quartz, the ore is practically smelted for nothing and the values recovered from an otherwise profitless material make its substitution more economical. The lining is rapidly destroyed by the union of the FeO, formed during the blowing, with the silica of the lining and the life of an acid lining is limited to about five charges, depending upon the grade of matte converted, a low-grade matte being more destructive than one of higher grade due to the larger amount of iron slagged. The great expense of frequently renewing the acid lining has led to its replacement by a lining of magnesite brick which is not attacked chemically by the process. When using such a lining the silica necessary to flux the iron in the matte is added to the charge before starting the blow. The basic lining is rapidly displacing the acid lining unless special considerations make it more profitable to retain the latter. The main advantage of the basic lining are: the decreased cost of lining, a basic lining producing 6,000 tons of copper as against 25 to 40 tons for an acid lining, longer converters can be used resulting in lower operating costs, and mattes of lower grade may be converted.

The operation of converting is conducted by first turning down the converter so that the mouth is in proper position to receive the molten matte from a ladle. The charge having been poured in, the blast at about 16-lb. pressure is turned on and the converter turned up until the tuyeres are below the surface of the matte and the mouth of the converter is under the hood conveying the waste gases to the stack. The oxidation commences and is divided into two stages, the first or slagging period, and the second or blister period. The reactions occuring during the slagging period are

$$FeS + 3O = FeO + SO_2$$
$$Cu_2S + 3O = Cu_2O + SO_2$$
$$Cu_2O + FeS = Cu_2S + FeO$$
$$2FeO + SiO_2 = 2FeO{\cdot}SiO_2$$

With the acid lining the FeO formed unites directly with the silica of the lining and on this account, as previously stated, it is necessary to have the matte as high grade as economically possible. A 30 per cent copper matte contains approximately 1.7 times as much iron as a 50 per cent matte and the lining will be consumed that much more rapidly. As an offset to the economy of converting high grade matte, there is the question of increased slag loss in the blast furnace or reverberatory when making high-grade matte and the question of the proper grade of matte to be made and converted depends upon local conditions but will average about 45 per cent copper. This condition does not exist to the same extent when using the basic lining as the siliceous flux is added to the converter before the blast is turned on.

As the oxidation proceeds and the iron is slagged the matte remaining in the converter gradually approaches white metal (Cu_2S). This change may be followed by the character of the flame issuing from the mouth of the converter. At the start of the operation it has a reddish color and, as the white metal stage approaches, changes to a pale blue. However, if an impure matte is being converted, the flame indications are unreliable and dependence is placed upon the appearance of the layer of matte on the punching rod which is inserted in the tuyeres to keep them open for the passage of the blast.

The iron having been slagged, the converter is turned down, the blast shut off and the slag poured or skimmed into a ladle. A fresh charge of matte, or matte and flux, is introduced and the operation repeated until sufficient white metal has accumulated in the converter for finishing. The converter slag contains several per cent of copper and is too valuable to waste and is, therefore, returned to the blast furnace or reverberatory for retreatment.

The second or blister period consists in oxidizing the sulphur of the white metal, the copper together with silver and gold remaining in the metallic state. The reactions during this period are

$$Cu_2S + 3O = Cu_2O + SO_2$$
$$2Cu_2O + Cu_2S = 6Cu + SO_2$$

The blast oxidizes the white metal to cuprous oxide which reacting with the sulphide liberates copper and forms SO_2. During this period the flame of the converter changes from a pale-blue to a reddish-brown but the appearance of the metal on the punching rod is a surer indicator and is invariably used. Upon the completion of the blow the converter is turned down, the blast shut off and the copper poured into a ladle for casting into molds.[1]

Copper produced in the converter is known as blister copper due to the appearance of the upper surface of the cast pig. It contains approximately 99 per cent copper, the balance consisting of sulphur and small amounts of impurities together with the silver and gold originally in the matte. It is too impure for commercial use and must be submitted to a refining process before it can be marketed.

THE SMELTING OF IRON

By Bradley Stoughton[2]

General Description.—Iron is found in the earth in the form of ore, or oxide, of which the commonest varieties are Fe_2O_3 and Fe_3O_4. The former is occasionally combined with more or less water. The smelting of these ores consists in heating them to a high temperature, first in contact with reducing gases (chiefly CO—which removes the greater part of the oxygen) and, finally, in contact with white-hot carbon, which completes the reduction. The smelting takes place in blast furnaces the form of which is shown in Figs. 11 and 12. The blast furnace itself is shown in Fig. 12, in section, and on the left of the picture in Fig. 11; while the four other furnaces in Fig. 11 are the so-called hot-blast stoves, which are used for the purpose of preheating the blast that is driven into the furnace for the

[1] The first copper formed carries down the great bulk of the gold and silver, and with matte carrying very little of these metals, so that when the bullion does not carry enough precious metals to make refining by electrolysis commercially advisable, selective converting is sometimes resorted to. The old Davids *selecteur* converter had a pocket to catch the first copper formed. The reaction is one worth remembering.—Editor.

[2] Consulting engineer, 1107 Broadway, New York, N. Y.

purpose of burning the coke and thereby producing the temperature and hot gases required for the chemical reactions and the melting.

In Fig. 13 we have an outline section of a furnace showing the temperatures and the typical chemical reactions predominant at each zone. A column of coke fills the body of the furnace from the bottom of the hearth to the widest portion, which is known as

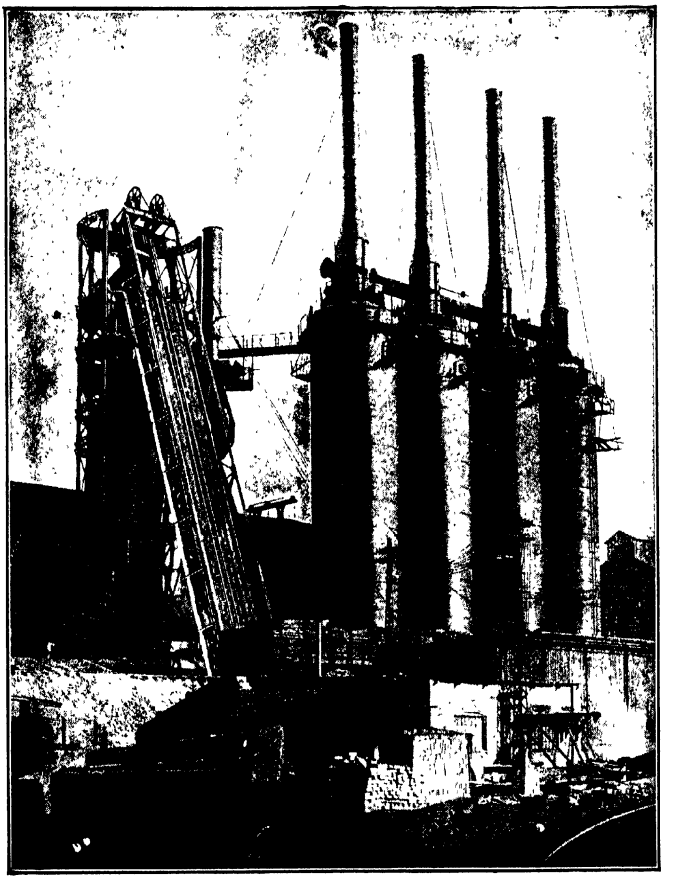


FIG. 11.—Iron blast furnace and stoves.

the top of the bosh. Above this "bed" are alternate layers of iron ore and coke, together with an appropriate flux, which is generally limestone, and which is introduced for the purpose of uniting with the impurities of the coke and the gangue of the iron ore, so as to produce a slag which will be fusible at the temperature of the smelting zone.

The preheated air, at a temperature of usually 800 to 1,200°F. (425 to 650°C.) and at a pressure of 15 to 30 lb. per square inch, enters through the tuyere pipes at the top of the hearth, combines with the fuel and creates a volume of intensely hot reducing

gases, which pass up through the interstices of the charge, heating, melting, and reducing the ore which it meets, and finally passing out the throat of the furnace.

The solid materials, consisting of ore, coke and limestone, are charged by mechanical means at the top of the furnace, and descend the 80 ft. to the hearth in approxi-

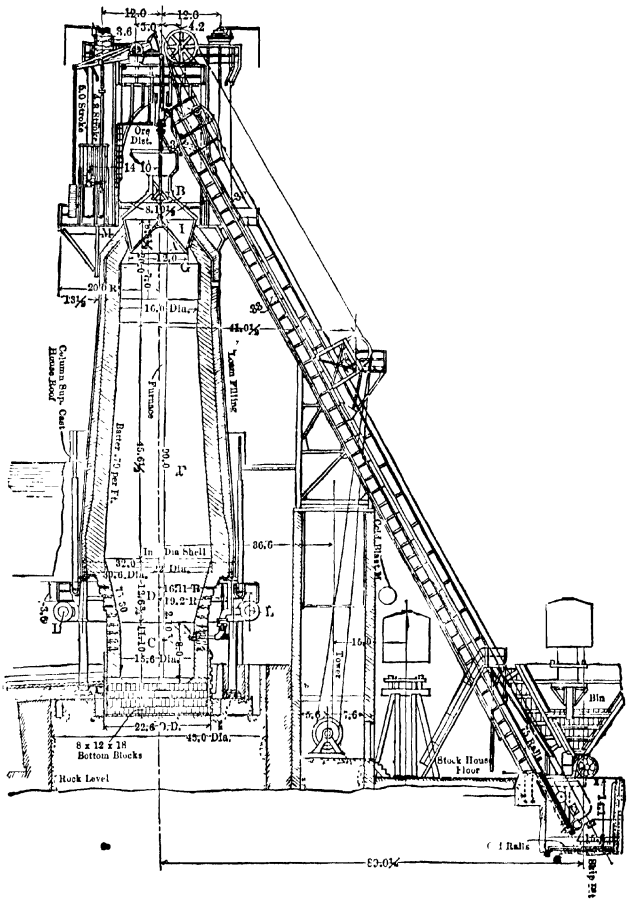


FIG. 12.—Cross-section of blast furnace and skip hoist.

mately 20 hr. The moderate heat met near the throat first removes any moisture present in the raw materials; then the CO gas begins to rob the ore of oxygen, until, about midway of the furnace height, the iron is all in condition of a metallic sponge, the interstices of which are largely filled with carbon in the form of a sort of soot, produced according to the reactions given in Fig. 3. The heat separates from the limestone its content of CO_2, which passes out through the off-take at the throat, with the other gases. When the descending solids reach the top of the

smelting zone, which is coincident with the greatest diameter of the stack, the temperature is sufficient to reduce them all to the liquid state, with the exception of the coke, which is infusible and which extends as a "bed" to the bottom of the furnace. This bed, plus the friction of the up-rushing gases, plus the friction against the furnace walls, is the support for the weight of the charge in the furnace.

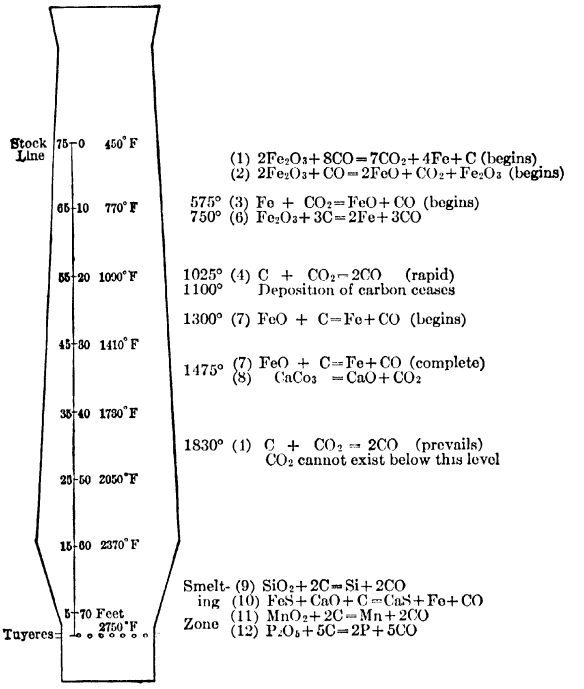


FIG. 13.—Diagram showing chemical action in blast furnace.

The Liquid Furnace Products.—The iron sponge melts above the top limit of the coke bed and trickles down, absorbing carbon, silicon, sulphur, phosphorus and manganese as described in the next paragraph. It collects in the bottom of the hearth and is drawn off at intervals by drilling a hole through the tapping notch. It is then either used in the fluid state at nearby steel works, or else is allowed to solidify in the form of "pigs." The slag also begins to form at the top of the smelting zone, by the union of lime with gangue of the ore. This too trickles down and completes its composition by dissolving the ash of the coke. This slag, or "cinder," floats on top of the iron and is drawn off through the "cinder notch," or "monkey," as often as is necessary to prevent its flooding the tuyeres. When very basic it may be used for the manufacture of portland cement.

Controlling the Grade of the Product.—The reactions in the smelting zone determine the chemical composition of the iron product, which is called "pig

iron," because of the form in which it is cast at old-fashioned types of furnace. The exact smelting zone reactions depend in turn upon the temperature of the smelting zone, and upon the constitution of the slag. Thus, the higher the temperature, the greater amount of carbon will dissolve in the metal; also the greater will be the amount of silicon reduced by carbon and the greater the amount of FeS[1] transformed into CaS. These reactions are important, because all the silicon reduced will go into the iron, and so will all the FeS, whereas CaS will dissolve in the slag. Therefore, a high temperature will mean—other things being equal—more carbon and more silicon in the iron, and less sulphur. On the other hand, a low temperature will tend to produce iron with low carbon, low silicon and high sulphur. The constitution of the slag is regulated by increasing or decreasing the percentage of lime put into it. Thus, a basic slag, high in lime, will tend to retain silica more tenaciously and resist its reduction to silicon. This action is important without being as powerful as the increased reduction of silicon with increased temperature of hearth. A basic slag will also facilitate the formation of CaS, and will yield more readily any manganese present in the charge, thus tending to decrease the sulphur and increase the manganese in the pig iron. These slag influences become most important in connection with the production of special grades of iron containing large proportions of silicon (10 per cent) and of manganese (up to 80 per cent). In general it is the temperature of the smelting zone which is the chief controlling influence, but it is also to be noted that a basic slag will increase the temperature of the smelting zone, because it requires a higher heat to bring it to that fluid condition necessary for the operation of the furnace.

Some analyses of typical slags, within wide limits of operation, are given below:

TABLE 1.—TYPICAL IRON BLAST-FURNACE SLAG LIMITS

	PER CENT
SiO_2[2] ..	20 to 70
CaO & MgO[3]	25 to 55
Al_2O_3[4] ..	5 to 20
CaS	Up to 4½
FeO	Up to 1

The constitution of typical grades of pig iron will vary somewhat as follows:

TABLE 2.—LIMITS IN ANALYSIS OF ORDINARY GRADES OF PIG IRON

	PER CENT
Carbon .	2 75 to 4.50
Silicon	0.75 to 3.00
Sulphur	0 30 to 0.02
Phosphorus	0 03 to 3 00
Manganese	0 20 to 1 00

Practically all the phosphorus that goes into the furnace with the iron ore (and, in less extent, with other raw materials) will be reduced and absorbed by the iron;

[1] The FeS gets into the furnace chiefly with the coke Rarely iron ores contain it.

[2] The silica comes from the ash of the fuel and the gangue of the ore, as well as that of the limestone.

[3] Lime and magnesia are chemically equivalent approximately, except that magnesia is about 40 per cent more powerful weight for weight.

[4] Alumina comes from the gangue of the ore and from the coke ash

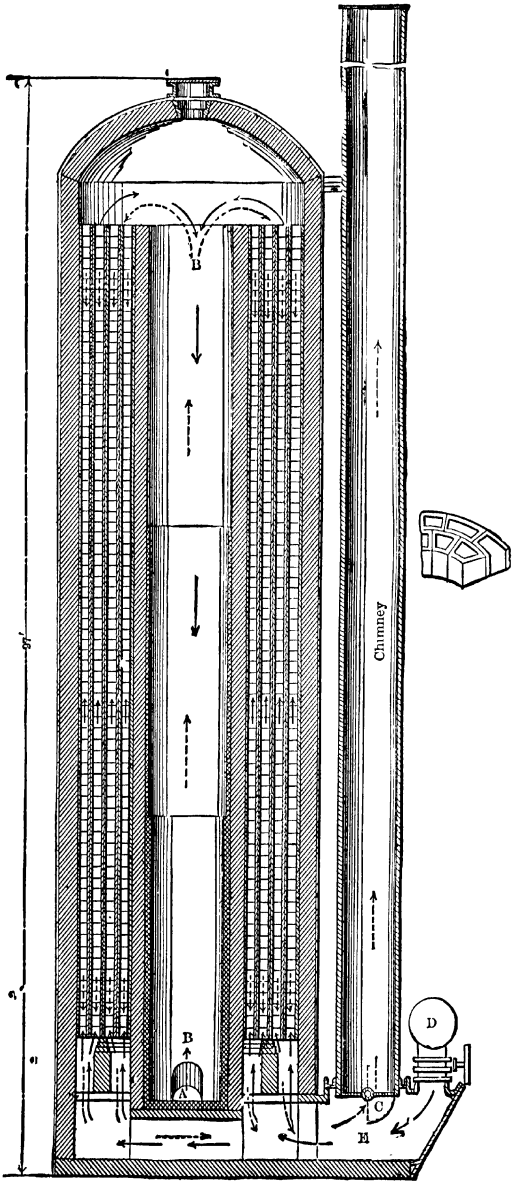


FIG. 14.—Hot-blast stove. From Howe, "Iron, steel and other alloys."

the same is true with manganese, except that an acid slag will carry away manganese oxide to partially satisfy its affinity for bases.

Controlling the Temperature of the Smelting Zone.—The all-important matter of the temperature of the smelting zone is determined by: the proportion of fuel used with the charge, known as the "burden" which the coke has to carry; the temperature to which the blast is preheated; and the basicity of the slag.

Preheating the Blast.—Modern furnaces have four "hot-blast stoves," and some very recent ones have even five. These stoves are heated by the waste gas from the blast furnace, which contains a little sensible heat, and which is a fuel by virtue of containing about 22 to 27 per cent of CO. It is drawn off at the off-takes; some of the dust is separated from it, and it may even be scrubbed clean. Then about one-third of it is burned in the stoves, and the remaining two-thirds is used to create power, by burning under boilers or in gas engines. One type of stove is shown in Fig. 4, the important feature being the large surface of brick exposed by the "checkerwork" construction, in order that it may absorb and impound heat from the burning gas. In a plant consisting of four stoves, three will be heating up in this way and one will be giving up its impounded heat to the air blast that is being driven into the furnace. A new stove is put on blast heating about once an hour. This is all regulated by the manager in proportion as he wishes to raise or lower the temperature of the air blast.

Dry Blast.—The most important and spectacular improvement in the iron blast-furnace process of the past few decades is James Gayley's use of dessicated blast. The moisture usually driven into the furnace with the blast cools the smelting zone by the endothermic reaction of dissociating the steam. Eliminating this reaction produces an effect in fuel economy greatly in excess of the theoretical amount of heat saved. This has been explained by J. E. Johnson, Jr., upon the basis that the operative heat of the furnace is the heat in excess of the minimum temperature at which the process can proceed. This operative heat is only about 100 to 200°; therefore an increase of 100° of hearth temperature might mean an increase of 50 or more per cent in heat efficiency.

Fuels Used.—Coke is the predominant blast-furnace fuel, and wood charcoal is the next commoner. Sometimes this is used because ore can be smelted economically where charcoal is cheap and coke is not; but more often it is because charcoal contains less sulphur than coke, and therefore pig iron with lower sulphur may be produced. The charcoal furnaces must be low in height, however, because the structural weakness of charcoal makes it incapable of supporting the weight of material that would prevail in the ordinary coke furnace having 100 ft. height. The use of anthracite coal mixed with coke is a commercial matter dependent only slightly upon the lower sulphur involved.

Other Processes of Reduction.—Iron ores occur in great quantity in many localities where coke is not available for smelting. Therefore electric smelting has been tried, in which charcoal is used in amount only sufficient for chemical reduction, and the heat has been furnished by electricity generated from water-power. In most cases the cost of the electricity and the small output in relation to the overhead cost has rendered these attempts commercial failures, although the technical operation of the processes has been successful.

Iron may be separated from its oxygen by the action of reducing gases below the melting point. This results in the production of an unmelted metal, usually in the form of sponge. The process is so easy and so economical of fuel that it has tempted many inventors, especially since it requires only liquid or gaseous fuel. The commercial stumbling block is that the product is only equivalent to steel scrap, which is usually abundant and cheap, even in many localities where coke is not available. Millions of dollars have been lost by men who have been influenced by the technical success of the processes, without understanding this simple commercial factor. However, the process may have a certain commercial value through the use of the iron sponge in isolated regions as a precipitant for copper in the hydrometallurgy of that metal.

SECTION XXV

CEMENTS AND GLUES

By S. S. Sadtler[1]

Classification.—There is a nearly infinite number of cements and they may be classified in various ways, but for convenience at this time they might well be subdivided into three classes: (1) Building cements, including portland or, so called, ordinary cement, Puzzolana, Rosendale mortar and hydraulic limes; (2) miscellaneous cements, or cements for other than building purposes, and lutes; (3) glues and casein preparations. The building cements I have considered under the section on "Materials of Construction" and the present section will treat only of classes (2) and (3).

The word cement connotes a more or less permanent bonding material while lute refers to rather temporary bonds. For instance, plaster of paris with water forms a cement, and glue and glycerine form a lute. For convenience in reference, cements and lutes will be classified by the uses to which they are to be put, though what is given here can only be a skeleton or outline of the innumerable number of possible combinations that will adhere or cause other substances to adhere after first mixing, by melting, evaporation or chemical union. In many cases better proportions of the substances given may be found and other fillers and binding agents will suggest themselves to the chemist or engineer.

Lutes are generally used to confine gases in or out and fresh portions are added as needed. It is not serious if there is a leak for more of the preparation can be applied. A luting compostition is chiefly selected to resist chemically the action of the gases or liquids, while cements are generally selected for a certain strength and durability. Cements are therefore more carefully applied. The surfaces to which they are to adhere are often roughened or scraped so as to promote adhesion. Sometimes they are painted with silicate of soda, neat cement, glue, shellac, etc., so as to give good contacts. Solder is rightfully a cement. A good operator tins the surfaces of the work after applying the flux, before putting the solder on in quantity. It might be mentioned here, for the few, perhaps, who do not already know, that solder in paste form is very convenient to use. It consists of finely divided solder mixed with a non-corroding flux and a lighted match often supplies enough heat to melt the solder and heat the flux sufficiently to cause it to clean the tarnish off the work so the solder can unite the surfaces.

Waterproof Cements.—As the chief waterproofing substances available we have the bituminous compounds, asphalts, pitches, gilsonite and blown petroleum residues, mixtures of these substances and mixtures of them with inert material. Candle pitch is an artificial bitumen that is tough and very sticky and much used for waterproofing. For instance, it is used as a waterproof coating between layers of cardboard.

[1] Chemical engineer, S. P Sadtler & Son, Philadelphia, Pa.

Of the asphalts, refined Bermudez is to be preferred as it is a nearly pure bitumen and forms homogeneous solutions with suitable solvents. A minor percentage of boiled linseed oil or blown petroleum oil is useful sometimes for tempering and fluxing. For solvent heavy naphtha is generally used. It does not dissolve all the asphalt, such as the so-called asphaltene portion, but it thins the asphalt very well. Coal-tar naphtha is better, however, at present it is slightly more costly. As voids are apt to form in a painted asphalt coating, some form of filler is generally employed, either by coating paper so that it becomes more or less impregnated or by the addition of a filler, such as silex or infusorial earth, to the asphalt.

For a soft, watertight coating in cement work, blown asphalt and infusorial earth, thinned with a solvent such as heavy naphtha, is employed.

The use of blown asphalts with natural asphalts and gilsonite is in some cases desirable, as the former are ideal fluxes for hard asphalts and tend to prevent brittleness or separation of the films when the solvent evaporates. The harder or higher melting point grades of these blown residuums are capable of making good cements alone or with filler, but are rather hard to dissolve. Such artificial asphalts have melting points as high as 150°C., while the softer ones that are probably best for fluxing have melting points about 80°C.

Testing of Bituminous Cements.—As to the choice of a suitable waterproofing substance for reservoirs, etc., we are chiefly guided by the experience of those who have constructed such works in the past and we seek from them information as to the materials used and are concerned their specifications for those materials. But in addition to this, certain small-scale waterproofing tests can be made by coating porous bricks with bituminous cements with and without fillers and noting the difference in weights, before and in given intervals after soaking in water.[1]

Lutes of boiled linseed oil, thickened with clay, asbestos, red or white lead, etc., are waterproof, but must be made thick enough from the filler added to resist mechanical action at the start. Linseed oil and whiting also make a good waterproof cement.

Flaxseed meal made into a stiff paste with water is useful as a lute for low-pressure steam connections and is easily applied. Portland cement only serves as a waterproof cement when given time for the preliminary setting to take place. It is not generally entirely impervious to water.

For all practical purposes the use of trade preparations, such as those containing metallic soaps or oil emulsions, serves to render concrete approximately impervious when the proper amount of water is used and the mass thoroughly puddled so as to eliminate voids.

For making small electrolytic cells it is desirable to use white iron-free portland cement and white plasterers' sand that has been sieved. If a 1 : 2 mixture is made with this sand and the prescribed quantity of an approved waterproofing substance, such as the product of the Newberry patent, aluminum oleate, Aquabar, Toxement, or the General Fireproofing Co.'s compounds, is added and care is taken to work out voids and the article in the *green* is kept moist, a waterproof container can be made which will stand dilute acids or aklalies, but not the two alternately. Of course acids act on the free lime, but silica is formed from the calcium silicate which tends to protect the preparation. When acids are to be used it is best to treat the finished

[1] The time of absorption of a given number of drops of water by a given amount of surface is also a fair guide as to the waterproof qualities of the solid.—EDITOR.

cell with hot paraffin unless the melting point of paraffin is below the temperature at which the cell is to be used.

Making Lutes with Portland Cement and Silicate of Soda.—A little silicate of soda in the water used with portland cements will help toward a quick initial set for under-water work. Water containing 2 to 40 per cent of silicate by volume causes a preliminary set in 2 hr. that prevents washing away by water. It injuriously affects the natural gradual hydration, however, unless the sodium hydroxide, carbonate or sulphate formed is washed out by excess of water, which is difficult to do. Mixtures containing above 4 per cent of silicate of soda show efflorescence, this is particularly marked when made with 20 per cent aqueous solutions of silicate. The silicate-of-soda-setting is at first due purely to double decomposition of sodium silicate and calcium hydroxide. If very strong silicate is used the mass stiffens so fast that it cannot be worked. This is true of all concentrations of 50 per cent or over.

Therefore for immediate immersion in running water silicate of soda acts as a binder, while the particles of the cement form gelatinous colloids instead of being washed away. The soluble sodium salts are then gradually more or less eliminated and apparently normal concrete results. Glue solution (3 to 5 per cent strength) with white portland cement insures very dense compositions, but the tensile strength is likely to be a little deficient. It is possible that the glue aids colloid formation, and protects the mixture against too rapid crystallization.

Oilproofing is often necessary to lute apparatus containing oil vapors or vapors of liquids immiscible with water. Glue or silicate of soda compositions are probably most used. A typical composition is: Good glue 2 parts by weight, glycerine 1 part, water 7 parts. The glue is first softened by the water, then liquefied by heat and the glycerine is incorporated. This is a good lute to render corks vacuum tight and for stopping small leaks of combustible gases and oil vapors.

A putty of molasses and flour has been found useful in laboratories and even in the works for oil vapors. A lute made according to the following proportions is very satisfactory: Glycerine 90 parts by volume, water 10 parts, made into a stiff putty with: Litharge 90 parts by weight, red lead 10 parts. It takes several hours to stiffen and about a day to set. This mixture was formerly used for luting in gage-glasses on low-pressure boilers.

Several cements of which silicate of soda is an active principle or the chief binding substance are as follows: Silicate of soda (about 30°Bé.) and whiting, made into a stiff putty. This slowly sets by drying if not by chemical action. If precipitated magnesium carbonate be used the setting is so quick that it is hard to use the mixture. If it is used, however, the silicate should be diluted to one-third to one-half ordinary strength.

Barium sulphate is often used with silicate of soda. The silicate should be about 30°Bé. If the mixture is heated the cement dries faster and thereby sets. There is no chemical action. A very strong and ultimately hard cement for a variety of purposes is made by incorporating hot glue solution with plaster of paris.

Acid Proofing.—The asphaltic preparations referred to under waterproofing are acidproof if other than basic fillers are used. There are also some good pro-

prietary acidproofing preparations on the market, but their compositions are not disclosed.

Black putty is made by intimately mixing equal weights of china clay, linseed oil and melted pitch. The ingredients must be anhydrous.

Rubber cements may have varying compositions, but the following are practically the extremes. Equal weights of rubber and boiled oil are taken; the rubber is first dissolved in carbon disulphide in the proportion of 4 c.c. CS_2 to 1 g. of cut-up rubber. Hot boiled linseed oil is then added. The solvent is not removed by evaporation until the paste is applied to the apparatus to be luted.

The other formula, to which reference has just been made, differs in having four times as much linseed oil and then fireclay or other filler, such as silex, is used: Crude, finely cut rubber 1 part, boiled linseed oil 4 parts, fireclay 6 parts by weight. If equal parts of fresh unvulcanized rubber are used the masses are so stiff that they should probably be used without filler. If as much as 4 parts of linseed oil are used considerable filler can be incorporated and made into a workable putty.

Melted sulphur with fillers of stone powder, cement, sand, etc., are used, such a mixture even being recommended for small electrolytic tanks. The following is used for hydrochloric acid vapors: Rosin 1 part, sulphur 1 part, fireclay 2 parts, by weight. Linseed oil (boiled) and fireclay stand most acid vapors.

Inert fillers in boiled oil stand acid vapors (even nitric acid): Silex 20 to 30 lb., flock asbestos 10 lb. are fed into a mixer, a little at a time, with 6 qt. of boiled linseed oil. There are numerous acid-resisting mixtures possible in which silicate of soda is used. This is because in spite of the strong basic character of silicate of soda, the silicate is superficially changed to colloidal silica, which continues the cementing work, at first effected by the silicate of soda. Barium sulphate, powdered glass, china clay, etc., are used with silicate of soda slightly diluted with water. A strength of about 30°Bé. is best.

For dilute hydrochloric acid one may use white china clay 1 part by volume, fine white sand or powdered quartz and sand 2 parts by volume. Mix thoroughly and work up with just enough silicate of soda, dilute with an equal volume of water to make a paste. This can be rendered more impervious to water by the judicious incorporation of organic colloids. If a little fine casein be incorporated with the silicate of soda in a mixer so that the mixture is quite smooth the mass is better. About 5 per cent of fine, dry casein powder is added, based on the weight of silicate. If fresh milk curd can be used, corresponding to the same dry weight of casein and allowance is made for the water contained, a mechanical mixer will not be needed.

Chlorine Resistant.—The most reliable is made with portland cement as the chief ingredient: Powdered glass 1 part, portland cement 1 part, silicate of soda 1 part. The last mentioned should be diluted considerably so as not to set too rapidly." Portland cement quickly reacts with silicate of soda, while the powdered glass and clay react more slowly but finally render the cement insoluble as regards its mass.

General Mixtures with Plaster of Paris.—This series of lutes and cements is highly important, and individual formulas are adapted to prevent the escape of hydrocarbon and other gases in furnace work, as cements for mechanical purposes and for wall coatings such as plaster. When mixed with asbestos, straw, plush

trimmings, hair, etc., the plaster of paris mixtures are physically strengthened or reinforced.

Some soluble sulphates form double crystallizable sulphates with calcium sulphate and water. They set harder and are more impervious than calcium sulphate (plaster of paris) alone. It is desirable not to take equal molecular quantities of the soluble sulphates to form the full double sulphates, but about half of these quantities. Sodium, potassium and aluminum sulphates are used for this purpose The two latter are preferable.

According to Sigmund Lehner, a little borax in the water used makes hard plaster cements and regulates the setting: 12 volumes of water to 1 volume saturated borax solution sets with plaster in 15 to 20 min. at 10°C.; 8 volumes water to 1 volume saturated borax solution sets in 1 hr. In another recipe, 1,500 g. of borax and 150 g. of magnesium oxide are melted together and powdered. This powder is then mixed with 75 g. of plaster of paris. Borate of magnesium thus predominates and protects the plaster from being washed away by water.

Marine Glue.—A standard preparation of this class of lutes (which are applied to crevices in a heated and fluid state, and become firm but not brittle when cold) is composed as follows: Crude rubber 1 part, shellac 2 parts, pitch 3 parts, by weight. The rubber is first dissolved in carbon disulphide or turpentine before mixing with the heated (not superheated) mixture of the other two. The advent of blown petroleum residuums has made it possible to make up hard but flexible compounds without rubber. Grahamite is a good base to which fluxes such as these just mentioned, or soft asphalts, are added.[1]

Gasket Compositions.—In the laboratory one can generally make out for low temperatures and pressures by saturating heavy "kraft" wrapping paper with soft pitch, such as wood pitch for steam or with gelatine and glue (hectograph composition) for oils. For high pressures, slots filled with lead rings and a V-shaped rim to the lid are most satisfactory. For large retorts asbestos rope and graphite are used for moderate pressures and lead for high pressures. Rubber compositions are most used for low temperatures where oils or solvents are not present.

Machinists' Cements.—These are the well-known red and white leads. The red lead is often diluted with an equal bulk of silica or other inert substance so as to make the mixture with oil less powdery on drying. One way to accomplish this is to add rubber or gutta-percha to linseed oil in the following way: Linseed oil 6 parts, rubber or gutta-percha 1 part, by weight. The rubber or gutta-percha is dissolved in sufficient carbon disulphide to give it the consistency of molasses. This solution is then mixed with the oil and left exposed to the air for about 24 hr. The red lead is then mixed to a putty. Oxide of iron makes less brittle cements than red lead. A portion of the red lead may be substituted by the cheaper red oxide of iron.

Leather Cements.—Equal parts of good hide glue and American isinglass, are softened in water for 10 hr. and then boiled with pure tannin until the whole mass is sticky. The surface of the joint should be roughened and the cement applied hot. Another is: One pound of finely shredded gutta-percha is digested over a water-bath with 10 lb. of benzol, until dissolved, and 12 lb. of linseed oil varnish

[1] Blown fish oil and blown cotton seed oil may also be used where quality is desired and expense a subsidiary consideration.—EDITOR.

stirred in. Still another cement is formed by melting together gutta-percha 8 oz., pitch 1 oz., shellac 1 oz., olive oil 1 oz.

Iron Cements.—When iron in a fine state of division, as in fresh oil-free filings or cast-iron borings that have been powdered, is mixed with an oxidizing agent, such as manganese dioxide or a substance electronegative to iron, such as sulphur, in a good conducting solution such as one of salt or salammoniac, galvanic action sets in very rapidly, ammonia is given off (if salammoniac be used) and the iron swells, by forming iron oxide, and cements the mass together. It is best diluted with portland cement. One formula is: Iron filings 40 parts, manganese dioxide or flowers of sulphur 10 parts, salammoniac 1 part, portland cement 20 to 40 parts, water to form a paste.[1] These cements are used extensively in foundries, etc. An odd application of the use of this cement is made in works that have quantities of iron in a more or less fine state, such as scrap from a magnetic separator. The iron is spread in layers, several inches in thickness, and is then moistened with salammoniac solution. Nature does the rest. The expansion of the iron, in forming oxide, knits the whole into a mass that forms good paths where it might otherwise be muddy in the yards of factories.

Crucible and Furnace Cements.—These cements for furnace linings are generally applied by hand. Sometimes air guns are used, however. For acid slags silica is most used and for basic slags magnesia, chromite, etc.

Silicate of soda and powdered glass or sand are suitable compounds for cementing lids on crucibles, etc. Sometimes the "iron cements" are used for such purposes, or iron filings and a little manganese dioxide are added to the above compositions for crucible cements. The first of these is the most practical for most purposes.

The best known cement for graphite compositions is fireclay, which with water binds the graphite fairly well and is used in making crucibles, muffles, etc. Carborundum powder is sometimes used with fireclay for furnace or crucible cement.

In some cases it is desirable to have an all-carbon binder, and for this purpose tars[2] or soft pitches are taken. Very little binder can be used, however, or the material will crack when heated, as the carbonizing of the pitch shrinks the binder somewhat. Starch paste has been recommended for this purpose, but the shrinkage is greater and the binding is not so good.

A strong, waterproof cement that will stand high temperatures may be made by mixing powdered silica or fine sand and powdered silica with a solution of magnesium chloride of about 10 per cent strength. This composition is applied as a putty and then painted or soaked in a solution of silicate of soda of about 30 per cent strength. This forms magnesium silicate as a binding material for the silica.

Magnesia composition for furnaces, etc., may be made by mixing magnesia burned at incandescent heat or hard-burned, 80 per cent and magnesia light burned (just sufficient to drive off CO_2 (560°C.), 20 per cent. The composition is made into a stiff putty with water and shaped as desired (or better still with magnesium-chloride solution, 18°Bé., if the cement is not to be heated to over 500°F.). The water must be driven off very slowly. A small proportion (3 to 6 per cent) of good asbestos fiber may be worked in to keep from cracking.

Oxy-chloride (Sorel) Cements.—These are sometimes called stone cements and the only one of practical importance outside of dental work is that made with magnesium chloride. If the magnesium chloride is quite pure, *i.e.*, free from

[1] The well-known "Smooth On" is such a paste.—EDITOR.

[2] If tar is used it should be the anhydrous variety, to obtain the best results.—EDITOR.

potassium, sodium or calcium chloride, the solution used need not be more than 19°Bé., but if commercial German magnesium chloride be used it requires a solution of 20 to 22°Bé.[1] The magnesium oxide must be freshly burned at a dull-red heat as the light oxide that is requisite for this cement readily absorbs carbon dioxide from the air and becomes unsatisfactory or of no use for making cement compositions. A diluent for the magnesium oxide is generally used, such as silica or wood pulp, ground wood, fine cork, infusorial earth, etc. Colors such as iron oxide and ochres are used, or anilines on a fuller's earth base.

The preparation is applied as a paste after mixing solids and the liquid. A good diluent is moistened portland cement as it tends to harden the mixture. This cement is said to have been used by the Germans in France and Belgium for emplacements for big guns instead of concrete as it sets much quicker. It is not entirely waterproof in itself, but can be rendered so. The biggest use is for floors, in stores, railway cars, etc. When wood meal or cork is used with, say, infusorial earth as a filler with the Sorel stone it makes a tough resilient surface that wears well and is less tiring to the feet than cement concrete etc.

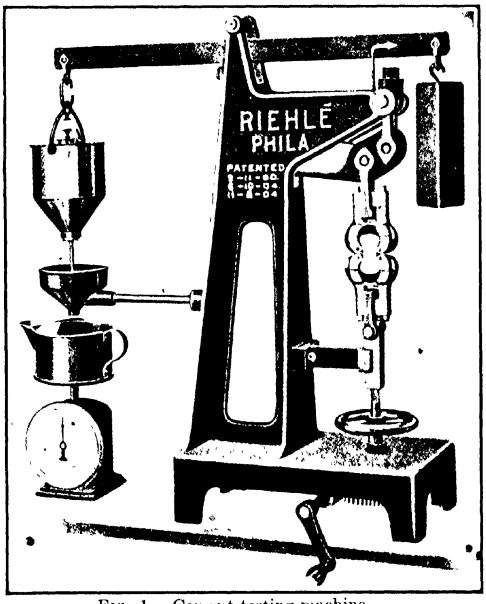


FIG. 1.—Cement-testing machine.

Testing in General.—Many of the cements treated on pages 940 to 943, and 949 to 951, may be tested as to strength by being made into test forms or briquettes and, after setting, pulled with a test machine such as shown above. Resistance to acids, alkalies, heat, oil vapors, steam, etc., are all tested in obvious ways by the use of the same test pieces. In all important work testing should be done.

[1] The figures, 27 to 30°Bé., frequently given, are wasteful of chloride.—EDITOR.

Glue.—There are several varieties of glue.[1] The most important are bone and hide glues, obtained from sources disclosed by their names. A fish glue is made from fish skins and offal, but is a cheaper grade and inferior for must purposes. It is generally met with as a rather badly smelling liquid. It is used by cabinet makers for certain purposes, where strength is not the great desideratum. Of course fish gelatin made from bladders of the sturgeon and other fish is a distinct and superior product. Liquid glue is made from high-grade hide glue by treating with strong acids such as nitric or hydrochloric. It has lost its power of gelatinizing but not its adhesive power.

Glue Testing.—Glue and gelatin occur in commerce in a great variety of forms (sheet, flake, shred, ground, powdered, etc.). While gelatin is usually colorless or else clear pale-yellow or brown, glue varies in color from milk-white to dark brown, and all possible shades yellow, transparent or opaque.

Although appearance[2] is no certain criterion of quality, glue is often erroneously judged by its color, clearness, fracture, etc. Since glue is used for a great variety of widely differing purposes, the *use for which the glue is intended* should always be borne in mind when subjecting it to test or technical examination. *A number of tests*[2] will, therefore, be given, *which may be conveniently run in consecutive series*, and their practical significance will be pointed out in a few instances.

Thin blown glasses about 3½ in. high and 2⅜ in. in diameter are convenient for making tests. Twenty-five grams of each glue to be tested is broken into small pieces and soaked in 100 c.c. of cold water until thoroughly softened. Thick sheet or flake glues must be soaked over night and should be allowed to stand in a cool place. With the glues under examination, there are at the same time soaked up a number of glues of known strengths (standards), for tests of glue should always be comparative. It is desirable and convenient to use the standards hereafter described (see page 850). With high-test glues, or in cold weather, less glue may be used, providing the unknown glues and the standards are treated exactly alike. In warm weather low-test glues must sometimes be tested 30 g. to 100 c.c. Gelatins are usually tested 10 to 100, or even 3 to 100.

When the glues are thoroughly softened, the glasses are immersed in a water-bath, and their temperature raised to 80° with constant stirring to insure complete solution. With thick-cut glues, care must be taken to see that no undissolved pieces stick to the bottom of the glass. The following tests are then made in the order given:

Reaction.—This is determined with strips of litmus paper. Where the degree of acidity or alkalinity is desired, a separate titration is made.

Viscosity or Running Test [2]—The viscosity is taken by running the hot glue solution at 80° from a pipette, and noting the time of efflux by a stop-watch. The relative viscosities are thus fixed in seconds.

[1] Glue in small oblong cakes (3 by 6 in.) is known as *Cologne glue*. *Scotch glue* is dark-reddish-brown, in large oblong sheets. *French glue* is generally about 9 in. square, and is frequently stamped with a trade-mark (*medal glue*). Glue opaqued with oxide of zinc is often called *Russian glue*, although in America thin-cut opaques are commonly known as white-shell glues. *Ribbon glue* comes in thin strips about 2 by 6 in., and *noodle glues* in thicker and narrower pieces. The dark, heavy noodle glue popular in Eastern countries is called *Bazaar glue*. The form in which a glue is dried or cut does not of course affect its quality.

[2] E. G. CLAYTON (*Journ.* Soc. Chem. Ind., 1902, Vol. **21**, p. 670) at the conclusion of a paper on the technical examination of glue says "while it would be rash to form a judgment on glue from a single test, the evidence afforded by a number may be irresistible. The expert's wisest system appears to be, not to rely upon single short-cut tests of general quality, but to employ a number of methods, including any having especial bearing on the prospective or present uses of the glue, and then base his conclusions on a consideration of all the results together."

The pipette adopted as standard has the following dimensions:

Capacity	45 c.c. of water at 80°C.
Internal diameter of effluent tube	6 mm.
External diameter of effluent tube.	9 mm.
Length over all of effluent tube..	7 cm.
Smallest diameter of outlet (about)	1 5 mm.
Outside diameter of bulb.. .	3 cm.
Length of bulb ...	9 5 cm
Length of upper tube	22 cm.

The pipette should permit the efflux of 45 c c. of hot water at 80° from the glue bath in exactly 15 sec. The viscosities of glues vary widely, as may be seen from the table of standards on page 850. Great care must be taken to make two pipettes that will give concordant results. The size and shape of the outlet hole, and the length and diameter of the effluent tube are the chief factors controlling the time delivery. The efflux hole is made by cutting the effluent tube square across, and holding it vertically in a bunsen flame with constant rotation. As the glass softens, the hole gradually draws together, and after a few trials can be brought to the desired size. It is desirable to have the lower graduation joint just where the effluent tube joins the bulb, for otherwise in glues of high viscosity there is much uncertainty caused by dribbling of the last few drops.

While running the pipette may be kept in a simple thermostat, consisting of a water-bath specially made for the purpose. The projecting effluent tube is protected by a mica cylinder through which the end point is observed. When the thermostat is used a small piece of rubber tubing controlled by a pinch cock is slipped over the upper end of the pipette, or a glass stopcock may be fused on.

After each determination, the pipette is washed out with hot water from the glue bath, and care must be taken that no undissolved glue, glue "skin," slime, or other obstruction clogs the outlet, even momentarily during use.

More complicated viscosimeters, as Engler's[1] or the Rideal-Slotte,[2] may be used, but they are cumbersome and slow of operation, and therefore impractical in routine work, where many determinations are made.

Odor.—To an experienced nose, the odor of the hot glue solution usually gives some indication of the raw material from which it is made. Decomposition is readily detected, although it is frequently masked by antiseptics or ethereal oils. Glues are rated as "sweet" or "off" as the case may be. With food gelatins, freedom from odor is essential.

Grease.—A brush-full of the glue solution is mixed with little aniline or other color, and painted out on a piece of white paper, when spots or "eyes" appear roughly proportionate to the amount of grease present. The grease is recorded arbitrarily on a comparative basis. For an exact estimation of fat in glue, etc., Kissling dissolves 20 g. of the sample in 150 c.c. of water containing 10 c c. of hydrochloric acid of 1.19 sp. gr. The liquid is heated for 3 or 4 hr. on a water-bath under a reflux condenser. The solution is cooled, 50 c.c. of petroleum-ether added, the liquid well shaken, and, after standing until clear, a known measure of the solvent is drawn off, evaporated, and the residue weighed.

Foam.—Foam is determined by agitating the glue solution with a rod or mechanical agitator and, like grease, is recorded comparatively. Some of the conditions affecting the foaming of glues are discussed by Trotman and Hackford[3] and H. J. Watson.[4]

[1] *Journ.* Soc Chem. Ind., 1890, Vol. **9**, p 654.
[2] *Journ.* Soc. Chem. Ind 1891, Vol **10**, p. 615.
[3] *Jour.* Soc. Chem. Ind., 1906, Vol. **25**, p. 104.
[4] *Ibid.*, p. 209.

Comparative Set.—The glasses are taken from the water-bath, and note is made of the comparative set or order in which the solutions gelatinize. In warm weather, especially with glues of low jelly strength, the glasses must be allowed to stand in ice water. As a rule, glues and gelatin gelatinize in order of their jelly strength.

Jelly Strength or "Finger" Test.—When the glue solutions have gelatinized, the glasses are arranged in order of the strength or resiliency of the jellies, as determined by pressure with the finger tips. Notwithstanding the personal equation, expert operators obtain much more uniform results than are given by the various mechanical devices.

Standards.—The selection of standards is of great importance, for once they are taken, all unknown glues are measured by them. Most published results of glue tests cannot be compared with each other, because of the great diversity of methods and glues used, and the absence of standards. That definite standards of jelly strength will simplify and harmonize the grading of glue is self-evident.

Sixteen arbitrarily established, nearly equidistant grades cover the usual range of jelly strengths. The grades are given values from 10 to 160, thus allowing 10 points between each grade. The following table gives the viscosities (as determined by the standard pipette, see p. 849) and the jelly strengths (as determined by Alexander's jelly tester) of these 16 standards. The determinations were made on solutions of the glues containing 25 g. of glue to 100 c.c. of water. For the standard viscosities there are taken the average of laboratory tests extending over many years, and inasmuch as standards of the same jelly strength are apt to vary in viscosity, there is indicated in the table the reasonable limit of such variation. Glues often greatly exceed these limits, but should not be chosen as standards.

Standards	Viscosities (in seconds) at 80°, solution 25 to 100	Allowable variation of viscosities (in seconds)	Jelly strength (in ounces) at 10°C.	Jelly strength (in grams) at 10°C.
10	15 ½	± 1 to 4		
20	16	± 1 to 4		
30	16½	± 1 to 4		
40	17	± 1 to 4	60	1,701
50	18	± 1 to 2	82	2,324
60	19	± 1 to 2	104	2,948
70	20	± 1 to 2	126	3,572
80	21	± 1 to 2	148	4,196
90	22	± 3 to 4	170	4,820
100	23	± 3 to 4	192	5,443
110	24	± 3 to 4	214	6,067
120	25	± 1	236	6,691
130	26	± 3	258	7,314
140	28	± 5		
150	34	± 8		
160	40	± 12		

The highest standards from 60 and upward should be neutral hide glues, clear, clean, well made, free from any odor of decomposition, and practically free from foam

and grease. For the lower standards, bone glues should be chosen, because most low-test glues are bone glues, and besides low-test hide glues usually have abnormally high viscosities.[1]

Water.—From 2 to 3 g. of glue are roughly granulated and dried at 110 to 115° until constant in weight. The estimation of water is without much practical significance if the glue is commercially *dry;* for the more moisture a glue contains, the weaker it will show on the viscosity and jelly tests.

Ash.—The ash of glue varies considerably, both in amount and composition. In the case of some bone glues the ash consists largely of phosphates, while in hide glues considerable calcium sulphate or other calcium salts (formed upon neutralization of the lime used in preparing the stock) are apt to be present. Chalk, clay, zinc oxide, and lead carbonate and sulphate, which are sometimes added as whiteners, and zinc sulphate, which is used as a preservative, are often found.[2]

For the estimation of ash, a weighed quantity (2 or 3 g.) of glue is incinerated in a large covered platinum crucible, using a few drops of nitric acid if necessary, to insure the oxidation of the carbon. The heating must be conducted with care, as the glue at first intumesces violently. The ash of bone glue is supposed to be fused by the heat of the bunsen burner, to be neutral, and to contain phosphoric acid and chlorides; whereas the ash from hide glue is supposed to be infusible owing to the presence of lime, to be alkaline, and generally free from phosphoric acid and chlorides.

The composition of the ash in reality depends more upon the nature of the process than upon the raw material used in making the glue, and from a practical standpoint its estimation is generally unnecessary, unless to detect some added adulterant or for the purpose of comparison. Hide and bone glues are frequently mixed, both in the liquor and in the finished form, and it is unsafe to attempt to judge the raw material of a glue on the basis of its ash.

Water-absorption Test (Schattenmann's Test).—A known weight of glue is immersed in water at ordinary temperature for 24 hr. In this time, the high-test glues absorb from 10 to 15 times their weight of water, whereas weaker glues absorb only 3 to 5 parts.[3] Very low-test glues form a slime rather than a jelly.

[1] Many American manufacturers and dealers use for comparative testing the so-called "Cooper grades" which were established many years ago by Peter Cooper, a pioneer American manufacturer, as grades under which his glues were sold.

A Extra	= Standard 130
1 Extra	= Standard 120.
1	= Standard 110.
1 X (called one cross)	= Standard 100.
1¼	= Standard 90.
1⅜	= Standard 80.
1½	= Standard 70.
1⅝	= Standard 60.
1¾	= Standard 50.
1⅞	= Standard 40.
2	= Standard 30.

In all probability, these were originally based upon the distance a certain weighted rule would compress a certain dish or bowl of jelly. The "No. 2" allowed it to sink 2 in., the "No. 1," only 1 in., while the intermediate grades were measured in eighths of an inch.

[2] It is probable that any crystalloid mineral compounds will affect the glue somewhat injuriously.

[3] S. Rideal soaks 10 g of the coarsely powdered sample of glue in water at 15° in a weighed beaker for 48 hr. At the end of this time the water is carefully decanted, and the increase of weight ascertained, the character and odor of the jelly being also noted. Good glues give a firm jelly, and absorb from 5 to 9 times their weight of water. In other cases, the product is not jelly but a slimy liquid. According to Kissling the amount of water absorbed by glue affords no indication of its cohesive power, and Fels describes it as an uncertain test. If the sample is finely ground or powdered, this test cannot be made.

H. R. Proctor (*Kolloidchem. Beihefte*, 1911, Vol. **2**, p. 243) found experimentally that the swelling maximum of gelatin is influenced by the volume of the original jelly from which it was dried. The presence of highly ionized acids enormously increases the water absorption of gelatin.

Although the best glues take up more water than inferior qualities when immersed in the liquid, well-made and well-dried glues are much less hygroscopic than badly made specimens, or than those prepared from inferior materials. The latter are also liable to undergo putrefaction on exposure to dampness.

The water absorption is roughly proportionate to the jelly strength, but it so inaccurate that it is hardly worth the trouble involved, unless as a rough approximation.

Tensile Strength of Glue.[1]—Many methods have been suggested such as Bauschinger's, Kissling's, and Rideal's.[1] Rideal has devised the following method: Two plane surfaces of biscuit porcelain, ground so as to fit, 1 sq. in. in area, are soaked with a solution made up of 1 part of glue in 2 parts of water at 70° for 30 min.; they are placed together, weighted with 5 lb. and kept for 5 days in a cool room. They are then fixed in a testing machine, and the weight necessary to tear them asunder is determined.

The writer has used with success a slightly modified form of a method originally suggested by Millar.[2] Ten per cent solutions of the glues to be tested are made up. Strips of filter or other paper are cut, 1 in. in width and about 18 in. in length. These are dipped in the solution at about 50°, and then hung up to dry. When the first coat has dried, they are again immersed in the solution and allowed to dry, the portion that was lowest being placed at the top, so that as far as possible a uniform layer of glue is produced on their surfaces. After air drying, the strips are heated for 1 hr. in the water-oven. Two or three lengths of 3 in. are cut out of the central portion of the strips. These are then separately tested by fixing between two indiarubber-covered clamps, one of which is fixed to the table and the other attached to the beam of a strong balance, the balance with the clamp, of course, being first counterpoised. Weights are added to the other pan until the paper breaks. A blank test is then made with the unsized paper, and this is deducted. Several experiments should be made, and the mean taken. A good glue should require some 9 or 10 lb. when tested in this way to break the sized paper.

Interpretation of the Results of Tests.—Glue is used for a multitude of purposes, and each line of work has its special requirements. Experience has taught that glue of certain characteristics made from certain kinds of stock will, in certain cases, do the best work at the lowest cost. It is, therefore, best to test unknown glues against those which are actually doing the work, and give the ones which show up well a trial under actual working conditions. If this is impossible, a laboratory test must be devised, in which the actual working conditions are exactly simulated; the more nearly this is done, the more valuable the test will be.

Practical Work with Glue.—The following precautions should be observed in practical work with glue in order to get the best results. The glue should be weighed and the water measured according to proportions already established, either by laboratory test or in practical work. The amounts should not merely be guessed at. The water and glue should then be mixed and stirred and allowed to stand in a covered vessel for at least 2 hr. It should then be heated carefully. About 140°F. is the best working temperature and it should never exceed 150°F.

The glue should not be heated longer than is necessary and for the highest type of work the glue should not be used after being heated for more than 8 hr. The

[1] "Dictionary of Applied Chemistry"—THORPE, 1912, Vol. 2, p. 750.
[2] *Journ.* Soc. Chem. Ind,. 1899, Vol. 16.

surfaces to be united should be dry and at least as warm as the air in the shop, which should be as warm and humid as the health of the operatives will permit.

Casein Preparations.—Casein is a protein substance obtained by drying the nearly fat-free curd of separator skimmed milk. It is a mild acid in its properties and combines with bases such as soda and ammonia and also with alkaline earths and heavy metal oxides. The usual substances employed to form soluble compounds with casein are soda ash, borax and ammonia.

Calcium, magnesium, aluminum, zinc and lead salts are used to precipitate casein as the corresponding insoluble salts. They are hard to form into colloidal masses, however, and it is more usual to make insoluble masses of casein with formaldehyde. Casein, besides being acid in its properties, because of its amino-groups acts like a weak base with acids and combines with certain quantities of sulphuric and hydrochloric and other strong acids.

Casein is usually precipitated with sulphuric or hydrochloric acid but "self soured" and rennet-precipitated casein are on the market and are better grades for some purposes. It is much used as a sizing or finish for paper, as a glue for veneers, etc., and for making horn or ivory-like substances for billard balls, cigar holders, insulating parts, etc.

Casein is often used in the form of sodium caseinate as it can be kept indefinitely as a dry powder, and when added to water makes a strong glue or a sizing preparation. Instead of using casein in this way, if sodium silicate is mixed to form a thick paste with finely powdered casein an especially strong glue is obtained. Doubtless sodium caseinate is formed in large part setting free colloidal silica. When the glue dries the composition becomes hard and strong.

The strongest and most insoluble glue made from casein is that developed for glueing the laminations of plane propellors and now used for veneering wood. It is insoluble when set and is not even loosened by steam. The principal requirements of casein to make it desirable for glue making are (1) that the percentage of impurities such as acid, moisture (not over 8 per cent) and fat (not over 1.5 per cent) must be small; (2) freedom from sour odors; (3) clearness and uniformity of color; and, (4) fineness of particles (less than 50 mesh). By grinding a casein to fine particles a minimum of time is required in the mixing and a more uniform glue is obtained. The ash should not exceed 3 per cent for natural sour, or 4.5 per cent for acid precipitated casein.

Manufacture of Casein Glue.[1]—To produce glue, casein is mixed with other ingredients, the chief of which are lime and water. These three constituents alone will give a glue of good water-resistant properties but of short life. Other ingredients are, therefore, added to increase the working life and the water resistance and improve the other qualities of the glue. Sodium hydroxide, sodium fluoride (patented) and sodium silicate are used in various formulas. They all lengthen the life of the glue and sodium fluoride probably gives the glue antiseptic properties. Still other ingredients are added to give the glue some particularly desired property. Oils are usually added to the dry-mix glue to prevent dusting in handling the glue. Formulas vary therefore, not only with reference to materials used but as to the proportions of different ingredients.

Several formulas for mixing casein glues have been developed at the Forest Products Laboratory. One of the best of these, with a discussion of the method of mixing and a description of materials required, is as follows:

[1] Taken from formulas devised by Forest Products Laboratory, U. S. Dept. of Agriculture.

GLUE No. 4-B[1]

Formula

100 parts casein
150 to 250 parts water } soak 15 min.

15 to 22 parts hydrated powdered (high calcium) lime
90 parts water } mix
70 parts silicate of soda (40°Bé.) } mix } mix

Method of Mixing.—The proper quantity of water is introduced into the glue pot and the mixing blade is brought into action at a speed corresponding to about 50 or 60 r.p.m. The stirring is allowed to continue during the addition of the casein to the water and for a few minutes thereafter until the mixture becomes mush-like in consistency, through the absorption of the free water by the casein; the blade is then stopped and the mixture allowed to soak.

After a period of 15 min. the soaking is considered complete and the mixing blade is again brought into action. The lime-water mixture is now added and 2 or 3 min. later the liquid silicate of soda is introduced. The mixing is allowed to continue for 20 min. to ½ hr. after the addition of the silicate of soda, whereupon a smooth freely flowing mixture of uniform texture and free from lumps should be obtained.[2]

Usually actual experience in the mixing of this glue is necessary before satisfactory results can be expected, and it is advisable to have a new operator witness an actual demonstration. This is due to the fact that no precise quantity of water can be prescribed because of the variation in the water-absorbing qualities of different caseins. The criterion of whether or not the proper quantity of soaking water has been added is the viscosity of the finished (mixed) glue. If its consistency is too thin an excess of water beyond that required has been used, and it is best to reject the batch and try again. Similarly, if the consistency is too thick and heavy an insufficient quantity of water has been used. The water required for various types of casein lies in the following ranges:

Lactic-acid casein	130 to 170 parts water per 100 parts casein.
Sulphuric acid casein Hydrochloric acid casein	170 to 220 parts water per 100 parts casein.
Rennet casein	280 parts water per 100 parts casein.

Galilith is the best-known horn or celluloid-like substance obtained by the action of formaldehyde on *casein* (from milk). The casein is dissolved in alkalis (such as caustic soda or aqueous ammonia), and the clarified solution is precipitated with acids, filtered, pressed, and dried slowly during some weeks or months. The plates so obtained, when soaked in formaldehyde and dried, form a yellowish-white translucent product, very tough like horn or ivory.

Casein Compositions Direct from Milk.—For many purposes, it is preferable to make casein as wanted direct from separator skimmed milk, as the homogeneity of the resulting colloid is greater. One hundred pounds of skimmed milk produces about 3¼ lb. of dried casein. The milk may be curdled with muriatic acid or rennet. The latter method is preferable for making casein for Galilith.

[1] U. S. Patent No. 1,291,396 on this process has been granted to Samuel Butterman of the Forest Products Laboratory and assigned to the United States Government

[2] The old household method of mending broken crockery by using the white of an egg mixed with lime is akin to this process. The cement produced in this way is a good one, but sets quickly. Good casein glues are now placed on the market by the Casein Manufacturing Co and Certus Cold Glue Co.—EDITOR.

The coagulation with rennet is effected at about 100°F. but with acid at 110 to 120°F. In both cases the coagulum after preliminary straining is heated to about 160°F. and strained and re-strained, or pressed. If diluents to make the goods opaque are put in they are best added before the coagulation as the resulting colloid in such cases becomes more homogeneous.

If transparent goods are aimed at, or very strong compositions are requisite, the following method, described at greater length in Scherer,[1] is to be recommended, as it eliminates the fat. Dissolve the casein (rennet) in sodium hydroxide, and then keep adding quite strong sodium hydroxide until all the casein is precipitated as sodium caseinate; it is then filtered off from the excess alkali containing the fat in a thin emulsified form. The precipitated sodium caseinate is dissolved in water, precipitated with the exact amount of hydrochloric acid necessary, and well washed. It is dried to the desired content of water (say 10 to 15 per cent) at low heat, pressed and treated with formaldehyde vapors for a considerable time to render insoluble. The relatively large amount of alkali in the filtrate can be recovered by causticising with lime, to be used over again.

The following recipes are often very serviceable to technical men: For cementing glass use 10 parts of gelatine in water mixed with a saturated solution of 2 parts of potassium bichromate. These two solutions should be mixed together and used in a subdued light. The compound forms an insoluble mixture quickly in the light. The so-called "cap cement," used by electrical instrument makers to fasten metal fittings to glass, is made as follows: Put 11 oz. of glue to soak over night in enough water to cover it. Next day add it and 1 oz. of white curd soap to enough water to make the total water 2 qt., the water being previously heated to boiling. To use, take some of the above mixture and add enough plaster-of-paris to make a smooth paste. Use quickly, for it soon hardens.

The well-known "universal wax," so useful in physical laboratories, is made by melting together beeswax, 4 parts; turpentine, 2 parts; then adding about 1 part Venetian red and working the latter in. The Venetian red may be varied somewhat to give differing consistencies. Cloth may be stuck to iron rolls using glue to which enough tannin has been added to give a ropy consistency. This must be used quickly. For sticking paper to metal use a solution of 2 parts gelatine and 1 of starch in the least quantity of water necessary to dissolve them.

[1] "Das Kasein" by ROBERT SCHERER, Vienna and Liepsig, 1905.

SECTION XXVI

RADIUM AND RADIOACTIVITY

By Richard B. Moore[1]

Discovery of Radioactivity.—The property of radioactivity was discovered partly by accident, by Henri Becquerel, the French physicist, in 1896. He was experimenting with certain fluorescent substances in order to find, if possible, a connection between fluorescence and the recently discovered *x*-rays. Among other chemicals which possess the property of fluorescence, he used salts of uranium. His custom was to expose the fluorescent substance to the action of the sunlight, and then register the effect of possible penetrating radiation on a photographic plate protected from ordinary light. Becquerel's experiments gave positive results at once, and he at first believed that he could discover a relation between fluorescence and *x*-rays. Later, he exposed a plate to uranium salts which had not been previously exposed to sunlight. To his surprise, on developing this plate he found that he had obtained the same effect as he had previously secured when the uranium salts had been exposed. The following up of this partly accidental discovery has given us our whole science of radioactivity. It was found that *radium and its salts* had the property of ionizing gases, or converting the molecules of gases into charged particles. It is this property which is used almost exclusively in identifying radioactive substances, and in making quantitative determinations.

Madame Curie's Work.—Madame Curie, wife of Pierre Curie, afterward Professor of Physics in the Sorbonne in Paris, became interested in the work of Professor Becquerel, and examined all the known elements to see whether any of them possessed properties similar to those of uranium. She found that thorium and its salts would also affect a photographic plate without previous exposure to sunlight, and would also ionize gases. Thorium as well as uranium is therefore, radioactive.

Madame Curie found that radioactivity was an atomic property. A given weight of uranium metal had the same activity, no matter whether it was combined with chlorine, bromine, the (SO_4) radical or the (NO_3) radical. The other elements in combination with the uranium did not affect the activity in any way. She then made a study of radioactive minerals, paying especial attention to pitchblende, which is a natural uranium oxide containing traces of lead, arsenic, bismuth, and other impurities. This was furnished her by the Austrian Government from its mines at St. Joachimsthal. To her surprise, she found that a piece of pitchblende carrying a given weight of uranium had approximately four times greater activity than any pure uranium salt containing the same weight of uranium. This indicated that either her original conclusion that radioactivity is an atomic property was wrong, or the pitchblende contained another element, or elements, which were also radioactive. She proceeded to test these conclusions and was assisted by the Austrian Government, which sent

[1] Chief Chemist, Bureau of Mines, Washington, D. C.

her a considerable amount of pitchblende for this purpose. The mineral was dissolved and the different groups of elements were successively precipitated, each precipitate in turn being tested for its radioactivity. The lead group was found to be slightly active, and we know now that this was due to the presence of radium D, or radioactive lead. The copper group was also active, due to the presence of polonium, which in many of its properties, is allied to bismuth. The activity associated with the iron group was due to actinium, which is allied to some of the rare earths. The majority of the radioactivity, however, was found to be concentrated in the barium, strontium, and calcium group. The separation of the small amount of highly active material found associated with these elements was diffi ult and tedious. On separating the calcium and strontium, the activity still remained with the barium; and the element, radium, was finally separated by fractional crystallization of its salts, either chloride or bromide, from the corresponding barium salts.

Other Workers in Radioactivity.—Madame Curie deserves great credit for the discovery of radium, and for a great deal of other scientific work she has carried out with marked success in connection with this element. But those who are not versed in the subject are likely to forget to some extent what has been accomplished by those who entered the field of radioactivity after the discovery of radium. Among those, Sir Ernest Rutherford, Sir J. J. Thomson and W. H. Bragg, stand out prominently on the physical side, while Sir William Ramsay and Professor Soddy probably lead on the chemical side of the subject.

Properties of the Rays.—Radioactive substances will affect a photographic plate and will ionize gases. This is due to the fact that radium and its salts give off three types of rays, called the alpha, beta, and gamma. The alpha rays travel with a velocity of about 20,000 miles per second and are positively charged. It was early found by Rutherford that their mass was comparable to that of a helium atom; and he definitely made the statement, before the proof was actually obtained, that the alpha particle was a helium atom with two positive charges on it. This was afterward proved by Sir William Ramsay and Professor Soddy, who dissolved some radium chloride in water and allowed the occluded gases to run into a spectrum tube which had previously been evacuated. On allowing these gases to stand for a day or two, the spectrum of helium gradually appeared.

The beta rays consist of negatively charged electrons, with a mass of about $\frac{1}{1600}$ of a hydrogen atom. During radioactive changes, they are ejected with a velocity of from 100,000 to 186,000 miles per second. While the alpha particle is stopped by an ordinary sheet of note-paper, the beta particle will penetrate a thin piece of glass, but is completely stopped by *a millimeter* thickness of lead. All evidence points to the fact that the beta particle is similar in its properties to the electron found in a Crookes tube, and gives rise to cathode rays.

The gamma rays are not material in character but are vibrations of very short wave length in the ether. Just as the x-rays are formed in an x-ray tube by the stoppage of the cathode rays by impinging on the target, so the gamma rays are formed during radioactive changes when such changes give rise to beta rays, and these rays are expelled from the atom with the velocity of light. It is evident, therefore, that the gamma rays are practically identical with the x-rays, except that they are of shorter wave length and penetrate matter to a much greater extent.

Anything, therefore, is radioactive which is undergoing atomic disintegration and giving off alpha, beta, or gamma rays, or all of them. All radioactive changes are accompanied by at least one of these rays. Their emission is due to the explosion of

the radioactive atom, such explosion taking place at a definite rate, so that in the case of radium itself one-half is completely transformed in 1,580 years. In the second 1,580 years, half of what is left will have been changed. In the third period of 1,580 years, half of what is left at the end of the second period will have been changed—and so on. The 1580-year period is called the half-life or half-value period of radium; and it can be readily seen that in 10 times the half-life period, less than 0.1 per cent of the element will remain unchanged.

Disintegration Series.—The manner in which radioactive elements change is shown in Table 1, giving the uranium series, and Table 2, the thorium series. Uranium 1, changes into uranium X_1 with the elimination of alpha rays; uranium X_1 changes into uranium X_2 with the elimination of beta rays; uranium X_2 changes into uranium 2 with the elimination of both beta and gamma rays—and so on down the list. It is thus plainly seen that the metal uranium is the parent of radium and, indeed, of all the radioactive elements which are found in any uranium mineral, and are shown in Table 1. Indeed, all of the elements of Table 1 are found in any uranium ore, and most of them can actually be separated chemically, and their physical and chemical properties identified.

It has already been stated that an alpha particle is a helium atom which has an atomic weight 4. Theoretically, therefore, whenever a radioactive atom explodes, with the elimination of an alpha particle, the resulting atom, left behind after the expulsion of the alpha particle, should have the atomic weight of the original atom minus 4, the atomic weight of the expelled helium atom. The atomic weight of radium has been determined experimentally as 226. The radium atom, during its change, loses an alpha particle with atomic weight 4 and, therefore, the residual radium emanation atom will have an atomic weight 222.

By examining the fourth column of Table 1, it is seen that whenever a change occurs involving an alpha particle, the atomic weight of the resulting element if reduced by 4. As the beta particle is an electron, it has not sufficient mass to affect the resulting atomic weight.

TABLE 1.—THE URANIUM RADIOACTIVE SERIES[1]

Uranium series	Half-value period	Rays	Atomic weight
Uranium 1	4.5 by 10^9 years	alpha	238
Uranium X_1	23.8 days	beta	234
Uranium X_2	1.15 min.	beta and gamma	234
Uranium 2	2 by 10^6 years	alpha	234
Ionium	9×10^4 years	alpha	230
Radium	1,580 years	alpha and slow beta	226
Radium emanation	3.86 days	alpha	222
Radium A	3.0 min.	alpha	218
Radium B	26.8 min.	beta and gamma	214
Radium C	19.5 min.	alpha, beta and gamma	214
Radium D	16.5 years	beta and gamma	210
Radium E	5.0 days	beta	210
Radium F	140 days	alpha	210
Radium G (lead)	stable		206

[1] The branches of Tables 1 and 2 are omitted for the sake of simplicity.

TABLE 2.—THE THORIUM RADIOACTIVE SERIES

Thorium series	Half-value period	Rays	Atomic weight
Thorium	2.2 by 10^{10} years	alpha	232
Mesothorium 1	5.5 years	beta	228
Mesothorium 2	6.2 hr.	beta and gamma	228
Radiothorium	2 years	alpha	228
Thorium X	3.65 days	alpha	224
Thorium emanation	54 sec.	alpha	220
Thorium A	0.14 sec.	alpha	216
Thorium B	10.6 hr.	beta and gamma	212
Thorium C	60.8 min.	alpha and beta	212
Thorium D_1	3.1 min.	beta and gamma	208
Thorium D_2 (lead).	stable		208

Experimental Proof.—There is some definite experimental proof that the above statements are correct. Sir William Ramsay and Professor Soddy actually determined the density of the radium emanation, and the figure obtained as a mean of five determinations was 223. In addition, lead is always found in uranium minerals, and the atomic weight of radium *G*, or the final disintegration product, according to theory, is 206. This does not coincide with the atomic weight of ordinary lead, which is 207; but some experimental work on the atomic weight of lead obtained from uranium and thorium minerals, by Prof. T. W. Richards, O. Honigschmid and Professor Soddy, has shown that the atomic weight of uranium lead is 206, while that of thorium lead is 208—an exceedingly interesting experimental confirmation of the theory. We have, therefore, actually three forms of lead, the only difference among them being their atomic weights all having exactly the same chemical and physical properties. If they were mixed by fusion, no known method could separate them; and the only way of telling one from another would be by making an actual atomic-weight determination.

The Actinium Series.—There is another radioactive series called the actinium series, which is very similar to the uranium series, but of less importance.

TABLE 3.—THE ACTINIUM RADIOACTIVE SERIES

Actinium series	Half-value period	Rays	Atomic weight
Protactinium	1,200 to 180,000 years	alpha	Not known
Actinium	20 years	(?)	Not known
Radio-actinium	18.8 days	alpha and beta	Not known
Actinium X	11.2 days	alpha	Not known
Actinium emanation	5.6 sec.	alpha	Not known
Actinium A	0.0029 sec.	alpha	Not known
Actinium B	52.1 min.	beta	Not known
Actinium C	2.1 min.	alpha	Not known
Actinium C_2(?)	(?)	alpha	Not known
Actinium D	4.76 min.	beta and gamma	Not known
Actinium E (unknown)			

The origin of actinium is not absolutely certain, but it and its disintegration products are supposed to be formed from uranium as a branch chain probably starting with Uranium 2. It is always found in uranium minerals.

RADIUM ORE DEPOSITS

Commercial Ores.—The two principal commercial ores of radium are pitchblende and carnotite. The former mineral has no definite composition, consisting of uranium oxides (UO_3, UO_2) with oxides of lead, calcium, iron, bismuth, manganese, copper, silicon, aluminum, and rare earths. Carnotite has a more definite composition, being a potassium uranyl vanadate containing small quantities of barium and calcium. The formula $K_2O.2UO_3.V_2O_5.3H_2O$ expresses its composition fairly well, although not exactly. Of lesser importance are autunite, a hydrated calcium uranium phosphate, $Ca(UO_2)\ 2(PO_4)_2.8H_2O$, and torbernite, a hydrated copper uranium phosphate, $Cu(UO_2)_2\ (PO_4)_2.8H_2O$.

St. Joachimsthal.—The pitchblende deposit at St. Joachimsthal, Austria[1]—is in mica schist interbedded with lime schist and crystalline limestone. Toward the east and northeast the formation is gneiss. The gneiss was intruded by quartz porphyry subsequent to the deposition of the vein material. In the mica schist are fissures filled with volcanic material which cut the mineralized zone at various points and depths. The veins are usually 6 in. to 2 ft. wide, in rare cases widening out to 3 ft. The mode of mineralization varies greatly, the ores occurring in both stringers and pockets. They contain the following metals: Silver, metallic and as argentite, polybasite, tetrahedrite, etc.; nickel, as nickelin, chloanthite, etc.; cobalt as smaltite, bismutosmaltite, etc.; bismuth, as metallic bismuth, bismite, etc.; arsenic, as metallic arsenic and arsenopyrite; and uranium, as pitchblende and other alteration products. Galenite, zinc blende, pyrite, marcasite, and copper occur in minor quantities.

The mines at Joachimsthal have been worked since 1517. In 1545 the production of silver ores declined considerably, but since then the deposits have been mined for bismuth and cobalt. During the last 25 years the mines have been worked for uranium.

Saxony.—In the vicinity of Annaberg, on the Saxon side of the Erzgebirge, the silver-cobalt veins resemble those at Joachimsthal. At Johanngeorgenstadt, the veins contain tin and silver-cobalt ores. Where dolomite spar is found, the silver-cobalt ores contain pitchblende, as at Annaberg. In the Gottessegen mine the pitchblende occurs in the spar in pieces 2 to 3 in. in diameter. These mines are worked principally for bismuth ocher, but also for cobalt and nickel.

In the cobalt-bismuth mines of Schneeberg are found bismutite and various minerals of nickel, silver, and arsenic. There is also some pitchblende, uranochalcite, uranospinite, galenite, zinc blende etc.

Cornwall.—Pitchblende has also been found in Cornwall, England in the tin region. As at Joachimsthal and Johanngeorgenstadt, the mineral is found associated with nickel-cobalt veins, although only part of the veins are highly

[1] RICHARD BECK: "Lehre von den Erzlagerstaetten," 3d. Ed., Vol. 1, pp. 408–410. Berlin, Borntraeger, 1909.—RICHARD BECK: "The Nature of Ore Deposits." Translation by W. H. Weed. 1st. Ed., Vol. 1, pp. 284–287. New York and London, Eng. and Min. Jour., 1905.

argentiferous. Even though these veins are closely connected with the tin veins, they apparently are not of the same age as the latter, but belong to the same general period of mineralization According to Ussher, Barrow and MacAllister, "The Geology of the Country Around Bodmin and St. Austell," Memoirs of the Geological Survey of England and Wales (1909), p. 157, the most important uranium producers are the South Terras mine, the Carharrack, Dolcoath, Wheal Unity, Wheal Gorland, Wheal Lovell, and Trenwith. The South Terras mine is situated in the valley of the Fal, southwest of St. Austell. The country rock is slate, intruded by greenstone and granite porphyry dikes.

Pitchblende in the United States.—Pitchblende has been found in the following localities in the United States: feldspar quarry, at Middletown, Conn., in large octahedrons; in Hall's quarry, at Glastonbury, Branchville, Conn., in a pegmatite vein and usually embedded in albite; at Marietta, S.C.; in the Baringer Hill District, Llano County, Texas; in the Bald Mountain district, Black Hills, S. Dak.; in Mitchell County, N. C.; and in Gilpin County, Colorado. The latter district is the only one of commercial importance.

All of the Gilpin County mines, with one exception, are found on or near Quartz Hill, a few miles from Central City. There are five that have produced pitchblende in quantity; the Kirk, Wood, German, Belcher, and Calhoun. The Kirk, Belcher and German mines are close together on Quartz Hill, the Wood and the Calhoun being in the valley below.

These mines, until recently, have been worked mainly for gold. In this district, gneiss and crystalline schist predominate, with intrusive andesitic dikes and occasionally acid granitic dikes. The rock containing the pitchblende, galena, sphalerite, etc., is a fine grained aplitic granite which probably once contained an appreciable amount of biotite. The ore deposits are of two general types, one containing pitchblende with pyrite, sphalerite and galena, and sometimes marcasite; the other type contains pyrite, chalcopyrite, sphalerite and galena, with some gold and silver. Generally speaking, the two types are not associated, so that the miner has a choice of mining either for pitchblende, or for gold.

The Kirk mine has probably been the most important producer of the five mentioned although reliable data on the output of pitchblende from this mine, up to a few years ago, has been difficult to obtain. During the last 12 years, about 20 tons of ore, with an average content of 35 per cent U_3O_8, and over 100 tons with a content of 3 to 4 per cent U_3O_8, have been mined. The mine has been shut down for some time. More recent operations of the German and Belcher mines produced 120 tons of low-grade ore, averaging about 1 per cent U_3O_8, and 6 tons of high grade. Smaller quantities of ore have been produced at various times from these mines and from the Wood and Calhoun, also the Joe Reynolds mine 5 miles west of Idaho Springs, Colo.

Australia.—Uranium ores are found in certain localities in Australia. One of these deposits is 80 miles east of Farina, a railroad station on the Great Northern line in South Australia, and lies between Mount Painter and Mount Pitt. H. L. Y. Brown[1] states that the rocks of the district consist of coarse and fine feldspathic, siliceous, and micaceous granite, gneiss, quartzite and mica schist. The rocks are contorted in places and penetrated by dikes of coarse, pink-colored eruptive granite.

[1] "Occurence of Uranium Ore and other Rare Minerals near Mount Painter, in the Flinders Range of South Australia." South Australia, Mines Dept. 1911.

Two of the prospect pits are on outcrops of iron oxide with cellular quartz and gossan, the whole having the appearance of an irregular lode. The uranium minerals, torbernite and autunite, are disseminated through the ore, and are also crystallized on the walls of the fissures and cavities in it. Uranophane and gummite occur sparingly; fergusonite and some monazite are also present. Another uranium deposit lies southeast of the one just described, about 20 miles southeast of Olary, on the railroad line from Petersburg to Broken Hill, South Australia. The ore occurs as a yellow and greenish-yellow incrustation and powder on the faces, joints and cavities of a lode, which consists of magnetite, titaniferous magnetite, etc., and quartz in association with black mica.

Portugal.—Autunite is found in commercial quantities in Portugal in the district between the towns of Guarda and Sabugal. An excellent description is given by Segaud and Humery.[1] Apart from the uranium, the rocks of the region are much mineralized, showing deposits of galena, arsenopyrite, chalcopyrite, tungsten and cassiterite.

Carnotite Deposits of Colorado and Utah.—All of the deposits referred to above are important and have been developed as commercial source of radium; in fact, until about 7 years ago, they were the only sources from which radium ores were obtained. About 1910, the carnotite deposits of southwestern Colorado and eastern Utah began to receive attention. They were known as far back as 1881, but the composition of the ore was unknown until 1897. In 1899, an analysis showed that the ore not only contained uranium, but was a potassium uranylvanadate.

In 1900, a small plant was erected in the McIntyre district, south of the Paradox Valley, Colo., for the extraction and recovery of uranium oxide from carnotite ore. Only moderate success was achieved, and the plant was shortly shut down. Operations were also started by other concerns, notably the Western Refining Co. and the Dolores Refining Co.; these plants extracted uranium and vanadium only. None of these operations was of importance, and it was not until 1909 to 1910 that any interest was shown in the carnotite deposits as a source of radium. At that time, the ore was almost exclusively shipped abroad.

In the fall of 1912, representatives of the U. S. Bureau of Mines made a thorough survey of the carnotite fields and announced the fact[2] that the carnotite deposits of Colorado and Utah constituted by far the largest source of radium-bearing ores in the world. Developments since that time have proved this statement to be correct, as the larger part of the radium that has been produced in the world has been derived from American carnotite ore.

The deposits are found mainly in Dolores, San Miguel, and Montrose Counties, Colorado, and extend over a belt about 60 miles long by 20 miles wide. The ore is also found to the west of the La Sal Mountains, in Utah, and along the San Rafael Swell, southwest of Green River, Utah. Small patches of ore are found scattered between these points and extend as far north as Meeker, Colorado.

The deposits are invariably pockets, many of which however, are of considerable size. A few individual claims have produced as high as 500 tons of shipping ore, which, however, is exceptional. The ore is found in a light-colored sandstone overlain

[1] Segaud et Humery. "Les Gisements d'Uranium du Portugal." *Annales des Mines*, Memoires, Ser. 11 (1913), 3, 111–118.

[2] RICHARD B MOORE and KARL L. KITHIL: "A Preliminary Report on Uranium, Radium and Vanadium." U. S. Bureau of Mines *Bull.* No. 70 (1913).

in places with shale and conglomerate; according to Hillebrand and Ransome, this is the McElmo formation.[1]

Amount of Radium in Ore.—Most of the radium obtained at the present time, as has already been stated, is obtained from carnotite ore. The average commercial grade of this ore contains from 5 to 10 milligrams of radium element per ton of ore. Some high-grade pitchblende ores may carry as much as 50 to 60 milligrams of radium per ton, but this is unusual. Allowing for losses in extraction and recovery, it takes about 5,000 to 6,000 tons of ore to give an ounce of radium element. It can be seen therefore, that the metallurgical processes involved in the extraction of radium are entirely different from those connected with any other element. There are two general steps which must be carried out; first, to obtain a radium concentrate from the ore; and second, the retreatment of this concentrate in order to extract a high-grade product. The first step is necessarily carried out on a large scale, while the major part of the second step is done in the laboratory.

Metallurgical Treatment.—Pitchblende was the first ore treated for the extraction of radium. This was done by Madame Curie who obtained her ore through the Austrian Government, from the St. Joachimsthal deposits. The original method used was to fuse the ore with sodium sulphate. This converted the uranium into sodium uranate. On washing with water the excess sodium sulphate and other soluble products were separated leaving the sodium uranate in the residue with most of the other heavy metals, sillica etc. The residue was then treated with dilute sulphuric acid which dissolved the sodium uranate and some heavy metals, leaving a residue which consisted very largely of silica, alumina, etc. The radium remained in this residue as radium sulphate. The acid solution carrying the uranium was treated for the recovery of this element while the residue carrying the radium was boiled with a solution of sodium carbonate. This treatment converted a portion of the radium sulphate into radium carbonate and sodium sulphate. The insoluble product was thoroughly washed free from sodium sulphate, and the residue treated with dilute hydrochloric acid. This dissolved the radium carbonate. The process of the boiling with sodium carbonate was repeated several times until all the radium sulphate was converted into radium carbonate and finally into radium chloride by solution in the hydrochloric acid. The mixed liquors were then added together and a small amount of barium chloride and sodium sulphate added in order to precipitate in the solution a definite amount of barium sulphate. The liquor was kept thoroughly agitated during the precipitation and practically all of the radium was precipitated with the barium sulphate. This product constituted a high-grade radium concentrate, and was refined by methods which will be described later on. In many ways still better results can be obtained by fusing the original ore with sodium carbonate instead of with sodium sulphate. After thoroughly washing, the residue, consisting of metallic carbonates and hydroxides, is dissolved in dilute chemically pure hydrochloric acid, and from this a high-grade radium-barium sulphate can be directly precipitated. If the ore is high-grade and largely free from pyrites it can be treated directly with boiling concentrated sulphuric acid. Radium sulphate is moderately soluble in hot concentrated sulphuric acid, and on diluting to a concentration of less than 10 per cent free acid the radium is precipitated as sulphate along with any barium and traces of calcium,

[1] W. F. Hillebrand and F. L Ransome: "On Carnotite and Associated Vanadiferous Minerals in Western Colorado." U. S. Geological Survey *Bull.* No. 262 (1905), 11.

etc., that may be present. This represents a crude concentrate which can be further refined. The American pitchblende ores cannot be handled in this manner because they contain a considerable amount of pyrites. The pyrite crystals have small particles of pitchblende embedded in them, and as the pyrite is not readily soluble in concentrated sulphuric acid, the radium recovery is poor. For the same reason fusion with sodium sulphate or acid sodium sulphate gives also a poor recovery. The American pitchblende ore is best treated by fusion with sodium carbonate or by the method used by the U. S. Bureau of Mines, *viz.*—boiling the ore with strong nitric acid until all the pyrite is decomposed, diluting, filtering and then treating the insoluble residue containing the radium with boiling concentrated sulphuric acid in the manner above described.

Carnotite.—The different methods of treating carnotite ore to obtain a concentrate may be classed under three general heads; (1) an alkaline leach followed by an acid leach; (2) fusing the ore with some material that will disintegrate it and make the extraction of the valuable contents possible; (3) an acid leach.

Alkaline Leach Methods.—It is probable that some of the early experimental work on extracting radium from carnotite ore involved boiling the ore with a solution of sodium carbonate, thus getting rid of the uranium and vanadium, which go into solution. Since radium has properties similar to those of barium, any radium in the ore would be converted into radium carbonate, and on treating the residue with dilute chemically pure hydrochloric acid, the radium would be dissolved with any other acid-soluble products.

The radium concentrate always obtained is radium-barium sulphate. By adding barium chloride and sulphuric acid, or sodium sulphate, to the slightly acid solution carrying the radium, barium sulphate is formed in the solution and drags down radium sulphate with it. The radium is almost always precipitated in this manner in a liquor sufficient in volume to hold it actually in solution. Undoubtedly adsorption has something to do with the precipitation of the radium along with the barium sulphate, but this does not fully explain the small losses that accompany such precipitation. The term "pseudo-isotopy" has been given to this property by Dr. S. C. Lind.[1]

The general principles outlined above are included in the Haynes-Engle process, which involves boiling the ore with an alkaline carbonate solution (see p. 864). The object of this process was to recover uranium and vanadium only, and did not attempt to obtain the radium in any form. A patent taken out by Warren F. Bleecker involved the extra step which the Haynes-Engle process did not cover, namely, the leaching of the residues with hydrochloric acid in order to obtain the radium in solution, after the ore had been boiled with an alkaline-carbonate solution.

The alkaline-leach method has many advantages and some disadvantages. It separates the uranium and vanadium from the ore during the first stage of the process. It eliminates sulphates by converting the metallic sulphates in the ore into metallic carbonates and soluble sulphates, which go into the filtrate with the uranium and vanadium. The radium, therefore, is left behind in the residue as carbonate, practically free from sulphates. This prevents the re-precipitation of the radium as sulphate, on treating with acid, until after the acid solution is filtered from the tailings. On the other hand, it has the following disadvantages: It converts some of the silica in the ore into sodium silicate, which makes filtration very difficult—in fact, most of

[1] S. C. LIND, J. E. UNDERWOOD, and C. F. WHITTEMORE: "The Solubility of Pure Radium Sulphate." *Jour. Am. Chem. Soc.*, (March, 1918) Vol. 40, pp. 465–472.

the filtering and washing has to be done by decantation. It is difficult to treat concentrates by this process, as these are almost invariably of very fine mesh, which adds to the filtration difficulties. The treatment with alkaline carbonate converts most of the iron and a good part of the aluminum in the ore into an acid-soluble form, so that the acid consumption is high. The method, however, can be used with success for the treatment of certain uranium ores, particularly carnotite, autunite, and torbernite.

Fusion Methods.—A treatment somewhat similar to the Austrian method for treating pitchblende, is given to the ores from Olary, South Australia, by the Radcliffe process. The main uranium mineral is carnotite, but this is associated with considerable quantities of ilsemannite and other rare-earth minerals that are not found in American carnotite. The concentrates are mixed with three times their weight of salt-cake, and fused in a reverberatory furnace; the fused product is then crushed and agitated in wooden vats, with water. By suitable adjustments it is possible to separate on the bottom of the vats a considerable amount of comparatively coarse material that is almost free from radium and uranium. The turbid overflow carries in suspension the radium, lead and barium, as sulphates, together with a considerable amount of finely divided silica. The overflow is pumped to large lead-lined tanks and allowed to stand all night. This is nothing but a sliming process and has the advantage that the radium in the form of sulphate always remains with the fine material. The slimes settle completely in 12 hr. and are collected periodically and treated for the recovery of radium.

The process of Schlundt, which is being used by one company in the United States in connection with carnotite, is very similar to the Radcliffe process. The ore is fused with acid sodium sulphate, leached and washed with water to extract the uranium, vanadium, and other soluble products, and the residue is slimed in order to obtain a crude concentration of the radium, which stays with the fine material.

The U. S. Bureau of Mines has found that if a radium-barium sulphate high in silica is fused with caustic soda containing a small quantity of sodium carbonate, the silica can be easily washed out as sodium silicate, while the barium and radium remain behind as radium-barium carbonates, which can be readily dissolved in hydrochloric acid. Usually the commercial caustic soda contains enough carbonate without the addition of any extra amount. This method has been applied commercially to the treatment of crude concentrates, such as are obtained by the Schlundt process.

One firm has used a sodium-carbonate fusion. The ore is fused with soda ash, usually about two and one-half times the weight of the ore being required. This is done in a reverberatory furnace, lined with magnesite brick, and the fused mass is run directly into vats, in which it is leached. The silica is thus converted into sodium silicate and so passes into solution, together with the uranium and vanadium. The iron, calcium, barium, radium, etc., remain as the insoluble residue, which is washed in filter presses. The material is then treated with dilute sulphate-free hydrochloric acid, which dissolves the carbonates, and the radium and barium are precipitated by the addition of the requisite amount of sulphuric acid, or sodium sulphate. The whole is allowed to stand in settling tanks and the clear liquid is drawn off, leaving the barium-radium sulphates mixed with a considerable amount of silica and other impurities, as a sludge at the bottom of the tank. This is taken out without previous filtration, and dried, forming a crude radium-barium sulphate which is then refined.

The main advantages of this method are that it will treat an ore containing considerable quantities of sulphates, as the process removes the sulphates as soluble sodium sulphate in a manner similar to the alkaline leach method. In addition it is

applicable to the treatment of concentrates, as fineness of material is really an advantage instead of a disadvantage, as it does not involve any "sliming." The main disadvantage is the cost, both for the chemicals and the labor required. The concentrate obtained is also low-grade, which involves additional refining costs.

Acid Leach Methods.—Leaching with hydrochloric acid gives an excellent extraction, provided the ore is comparatively free from sulphates. As a considerable proportion of such ores contain traces of gypsum, it is a method which must be used on selected ores. A hydrochloric acid leach has been used successfully on Cornish pitchblende, which is practically free from pyrite, but is not applicable in any way to American pitchblende, which contains considerable quantities of pyrite. It has also been used on Portugese autunite. In general, the hydrochloric method has a limited use.

Leaching with nitric acid has been used more successfully. This is the method originated by the U. S. Bureau of Mines[1] and used in the plant of the National Radium Institute. As is generally known, barium sulphate is much more soluble in nitric acid than in hydrochloric acid, and this is especially true when the nitric acid is concentrated and hot. For this reason, ores containing sulphates can be treated by a nitric acid leach, and the method has been successfully applied to ores carrying as much as 1 per cent gypsum. On ores carrying small quantities of sulphates, the extraction obtained is very high, frequently going, on a commercial scale, to 93 and even to 95 per cent. Boiling, 40-per cent nitric acid is used, and filtration is obtained on either a vacuum or a pressure filter. Filtration must be done rapidly, because as the acid cools, the radium has a tendency to precipitate out, especially in the presence of sulphates. During the process of recovering uranium and vanadium by this method, practically nothing but sodium hydroxide and sodium carbonate are added to the nitric acid. Consequently, sodium nitrate is obtained as the final product after the precipitation of the radium, uranium and vanadium, and this sodium nitrate is recovered by evaporation and crystallization and used over again for the manufacture of nitric acid in the ordinary way. The average losses of nitric acid were about 15 per cent, so that 85 per cent of the acid used was recovered as sodium nitrate. This actually reduced the cost of the nitric acid below that of hydrochloric, and this, together with the high extraction of the radium obtained, was largely responsible for the low cost of the recovered radium and the success of the method.

The process cannot treat successfully ores carrying as large quantities of gypsum as canbe treated by some of the other methods, such as the sodium carbonate fusion, but it is applicable to a very large percentage of the carnotite ore produced. Difficulty was experienced in treating concentrates, most of which are below 150 mesh. As already stated, it has been necessary to filter rapidly in order to get a good extraction; and the problem of filtering a 40-per cent boiling nitric solution, containing fine material in suspension, was found to be difficult. It was finally overcome by the development and use of a pressure filter instead of a suction filter; this consisted of a steel shell containing an earthenware filter set in concrete. The earthenware filter had at its bottom, as filtering medium, a plate of either filtros or alundum. The steel top was made tight with swing bolts, and a pressure of 100 lb. was applied.

Refining.—After the radium-barium sulphate is obtained, it is necessary to change this insoluble product into soluble form so that the radium can be fractionated from the barium. The old method of converting the insoluble sulphates into soluble chlorides consisted in boiling the radium-barium sulphate

[1] CHARLES L. PARSONS, R. B. MOORE, S. C. LIND, and O. C. SCHAEFER "Extraction and Recovery of Radium, Uranium and Vanadium from Carnotite," U. S. Bureau of Mines *Bull.* No. 104 (1915).

with a strong solution of soda ash so that the sulphates were converted into carbonates. After the first treatment, the insoluble residue, which consisted of a mixture of sulphates and carbonates, was thoroughly washed so as to free it from soluble sulphates, and was then leached with dilute chemically pure hydrochloric acid. This dissolved out the radium and barium carbonates which went into solution as chlorides, leaving the insoluble sulphates which had not been converted into carbonates by the first treatment. The process was then repeated; the sulphates being boiled a second time with soda ash, washed and leached with hydrochloric acid. Three or four treatments usually served to convert all of the sulphates into carbonates, which were ultimately obtained in the form of soluble chlorides by adding hydrochloric acid. All the acid liquors were then added together for fractionation purposes. It can readily be seen that this method involved a considerable amount of time and trouble and added considerably to the cost of radium production.

Reduction with Coal Gas.—It is a well-known fact that barium sulphate can be reduced by heating in a current of coal gas. A temperature control within reasonably narrow limits is necessary in order to get proper reduction, and at the same time to obtain the material in a non-clinkering condition so that it can be readily removed from the tube in which it is heated. This temperature control is the main objection to this method, as it is difficult to obtain fairly satisfactory results by heating with coal, oil or gas, and it is not easy to build an electric tube furnace which is suitable for the reduction. With coal gas, reduction begins at about 575°C.; the actual working temperature being between 725 and 740°C. The gas consumption averages from 200 to 300 cu. ft. for 25 to 28 lb. of sulphate. The heat of reduction is positive at high temperature, producing reaction clinkers, some of which are friable and some glassy and hard to break. With a high-grade sulphate, reasonably free from silica, the reduction varies from 75 to 90 per cent. If a considerable amount of silica is present, the reduction is decreased. The barium-radium sulphides obtained are dissolved in dilute hydrochloric acid and the solution filtered from unreduced sulphate. During the reaction with the acid, there is a copious evolution of hydrogen sulphide so that the work must be done outdoors or in a strong draft of air. The solution of barium-radium chlorides thus obtained is ready for fractionation.

A more satisfactory reduction of the sulphates to sulphides can be obtained by using charcoal instead of coal gas. The sulphate is mixed with about one-fifth its weight of powdered charcoal and heated for 7 or 8 hr. in a graphite crucible in an oil furnace at about 800°C. Reduction takes place readily, according to the equation:

$$BaSO_4 + 4C = BaS + 4CO$$

The crucible is covered with a lid, but a small opening is left at the spout at which the carbon monoxide burns. When the evolution of gas is complete, the crucible is allowed to cool with the lid on, and the radium-barium sulphide is removed and broken up. Under such conditions, with a sulphate reasonably free from silica, it is usual to get a 90 per cent reduction of the sulphate to sulphide; the ratio of the reduction of the radium being about the same. The sulphide is then dissolved in dilute hydrochloric acid; the whole is thrown on an earthenware suction filter, and the unreduced sulphate thoroughly washed with distilled water. This unreduced sulphate is either reduced a second time separately, or mixed with a fresh batch of the sulphate. The

ratio of radium to barium in the unreduced sulphate is about the same as in the original sulphate, but there is a greater concentration of impurities, such as lead. After these impurities have accumulated, it is more convenient to fuse the final product obtained with sodium carbonate. During this fusion, the lead accumulates at the bottom of the melt as metallic lead, and in this way is eliminated. The carbonates are dissolved in hydrochloric acid.

Plant Crystallization.—The liquor obtained from the above procedure will probably carry in solution radium and barium chlorides in a ratio of about 1 part of radium to 1,000,000 of barium. The only efficient method of separation of these two elements so far discovered is fractional crystallization. Radium chloride is less soluble than barium chloride and, therefore, will tend to concentrate in the crystals, whereas the barium will concentrate in the mother liquor.

The crystallization factor in hydrochloric acid solution is about 1.5 to 1.6; that is to say, if 50 per cent of the barium chloride is removed, there will be 50 per cent more radium in the crystals removed than in the liquor left behind.

The crystallization factor in neutral solution is considerably less, therefore, it is advantageous to crystallize in an acid solution. Acidproof ware of some kind must be used; and, as the volumes of liquor obtained from the plant are at first large, it is necessary to have vessels of considerable size. The most satisfactory vessels to use are steel or cast-iron pots with acidproof fused silica lining. Steam-jacketed vessels of 50 to 80 gal. capacity can be obtained of this material, and, if used carefully, will last a considerable time. The method of crystallization is as follows:

About six evaporators are required. The radium-barium chloride solution in the first evaporator is concentrated so that on cooling one-half of the barium chloride crystallizes out. This is richer in radium than the barium chloride in the original solution. The liquor is siphoned into evaporator No. 2, and the process repeated; one-half of the remaining barium chloride being allowed to crystallize. This procedure can be continued all the way down the series, or a fresh batch of liquor may be introduced into the first pot after the crystals have been removed. It is advisable to establish a permanent crystallizing system so that fresh liquor can be introduced each day into evaporator No. 1 and a batch of crystals richer in radium can be taken out each day for further refining. The system may be established in several ways: Either by adding fresh material to the first pot each day and gradually working the mother liquor down the evaporators to the bottom of the series; or by crystallizing the first batch of liquor introduced into the first pot all the way down the series before the introduction of fresh material. Whichever method is used, the procedure afterwards adopted is the same. Half of the barium chloride in No. 6 evaporator is crystallized out and removed from the mother liquor. This liquor should be very low in its radium content; carrying not more than 25 or 30 parts of radium per billion of barium. It is discarded. After the crystals have been removed from the evaporator, the liquor obtained from a similar crystallization in pot No. 5 is siphoned into No. 6, and the crystals from No. 6 are dissolved in this liquor. In other words, the crystals from each evaporator ascend and the mother liquor at the same time descends; the crystals from a given evaporator being dissolved in the liquor from the second evaporator above. The crystals taken from pot No. 1 can be further concentrated by giving two or three additional crystallizations before being sent to the laboratory for final refining.

Laboratory Refining.—The crystals obtained from a plant refining should contain from 5 to 10 parts of radium per million parts of barium. The salts of most metals, such as iron, aluminum and vanadium, that may occur with the

radium-barium salt as impurities, pass into the mother liquors, and only small traces remain with the crystals. Lead is an exception, however, and requires special treatment. Where barium-radium sulphide, after reduction from sulphate, is dissolved in hydrochloric acid solution with copious evolution of hydrogen sulphide, one might expect the almost complete removal of the lead content This does not occur, however, and some lead always remains with the crystals obtained from the plant crystallization system and must be removed later on. The crude barium-radium chloride received from the plant is dissolved in water in large porcelain dishes, and hydrochloric acid is added to precipitate as much lead as possible. After the solution has stood over night, it is filtered to remove the lead chloride and whatever carbon and barium sulphate may have escaped previous filtration. All filter papers used must, of course, be retained and afterwards ignited for recovery of the radium retained by the papers. The laboratory crystallizing system is very similar to that used in the plant, except the volumes of the dishes are much smaller and there are at least four vessels on the minus side and whatever number is required on the plus side to bring the refined salt up to the purity desired. If the crystals from the plant contain not more than 5 or 6 parts of radium per million of barium, four crystallizations on the minus side are usually sufficient to reduce the radium low enough so that the tails can be put back into the plant crystallizing system. No. 5 vessel, therefore, counting from the minus end, is the one into which all fresh charges of liquor are placed; and from this point the radium travels up the plus side and becomes more and more concentrated, and the barium travels to the last vessel on the minus side, from which point it goes back with whatever radium it still retains to the plant crystallizing system.

The vessels in which the actual crystallization is carried out may either be of silica, porcelain, or steel, lined with acid-proof material. The vessels in which the higher grade material is crystallized should always be of quartz. The procedure is the same as in the plant crystallizing system; for example, the crystals from pot No. 6 are dissolved in pot No. 7 in the mother liquor obtained from pot No. 8. As the factor of enrichment of radium chloride from barium chloride and also of radium bromide from barium bromide is more favorable in acid than in neutral solutions, a fair acid concentration is maintained throughout the chloride and also the bromide system which is afterwards obtained.

Removal of Lead.—The chloride crystals from vessel No. 2 on the plus side are dissolved in water without acid, and placed in a large glass precipitating jar 16 or 18 in. high. Make ammoniacal and pass in hydrogen sulphide until the precipitation of lead as lead sulphide is complete. This sulphide is filtered and collected and may be analyzed for its radium content. It should be stored for recovery of the radium by fusion with sodium carbonate. Attempts to precipitate the lead as sulphide even from slightly acid solution usually result in obtaining a brick-red precipitate of the formula $(PbS)_x . PbCl_2$ which is far more soluble in acid than lead sulphide; hence, complete precipitation of the lead is possible only in ammoniacal solution. If the solution is made alkaline with ammonia before passing in the hydrogen sulphide, only a small amount of radium is precipitated with the lead, usually not more than 0.2 per cent.

Conversion to Bromide.—Into the filtrate from the lead precipitate, powdered ammonium carbonate is introduced gradually with vigorous stirring until all

the barium has been precipitated as carbonate. After standing over night for the settling of the barium carbonate and the thorough precipitation of the radium carbonate, the supernatant solution is siphoned off as far as possible and the rest is thrown on a Büchner funnel where it is filtered and washed several times with distilled water. The filtrate which carries only small traces of radium is stored and may be returned to the plant at some convenient point before the precipitation of the radium. The amount of radium in the liquor is surprisingly low, usually 0.001 to 0.003 mg. per liter. The barium-radium carbonate is removed from the Büchner funnel and is dissolved in chemically pure hydrobromic acid of 20 to 35 per cent strength in a large glass precipitating jar. Fractional crystallization is now continued in silica vessels in fairly strong hydrobromic acid solution in which the separation factor is now 2 instead of 1½ as is the case for the chlorides. Crystallization, therefore, takes place more rapidly, but greater care in handling the vessels is, of course, necessary on account of the higher radium concentration. Heating may be carried on on tripods with bare gas flames until the richer fractions are reached, when the evaporation is carried out on an electrically heated water bath in which only distilled water is used. In case of an accidental loss of radium solution into the bath, all the water can be drawn off and returned into the system just before the treatment with hydrogen sulphide.

The evaporation required to obtain a suitable batch of crystals may be generally regulated by concentrating the solution until vigorous fanning just begins to cause the formation of crystals on the surface of the hot solution. Of course, the higher the acid concentration, the more generous the crystal batch will be, and it is usually convenient to have the acid concentration such that about half of the barium in solution will crystallize out. Owing to the high factor of enrichment as bromide, the radium content of the mother liquor from the "minus two" bromide vessel is extremely low. In general, the amount of radium returned to the plant in this bromide mother liquor is only about 0.2 per cent of the total amount going through the system. If such a result is actually obtained, it is more convenient and economical to use the bromide mother liquor for the recovery of hydrobromic acid than to return the mother liquor to the plant to recover its small radium content.

Number of Fractions Employed.—The number of fractions employed in the plus direction in the bromide system varies with conditions; 10 to 12 being the usual number. The crystallization is conducted in such a way that the barium bromide collected in the final fraction should not fall below 1 per cent of radium bromide, and sometimes is as high as 3 or 4 per cent. The total weight of the fraction should be 1 to 2 g. This fraction, after thorough drying in a hot-air oven, is sealed in a glass tube and kept for final purification, when a sufficient number of tubes have been accumulated. The amount of radium in the tube can be easily determined by means of the gamma-ray method, to be described later on. After 20 or 30 tubes have accumulated, they are opened and the contents dissolved in hydrobromic acid in a small silica dish.

If there is any considerable difference in the activity of the salt in the different tubes, it is wiser to put those together which have approximately the same activity for the initial solution, and to put those of higher activity in plus 1, plus 2 or plus 3 dish, depending upon the amount of radium present. Crystallization is then continued with a general tendency to push up the radium from the lower fractions into

the last silica dish in which the majority of the radium is finally accumulated. After thorough drying in a hot-air oven to free the salt from moisture and from water of crystallization, it is placed in a glass tube and hermetically sealed. In this tube a small platinum wire is sealed through one end in order to conduct away the unipolar charge that may collect in the interior, attaining voltages that could cause destructive sparking. Reports are on record of serious radium losses having resulted through neglect of this precaution.

RADIUM MEASUREMENTS

Measuring Instruments.—The methods used for determining the amount of radium in either an ore, or in a product such as a concentrate containing radium, depend entirely upon the fact that radium and other radioactive substances ionize gases. Such ionization is due to the alpha, beta and gamma rays which are emanated by radioactive substances. The methods are, therefore, entirely physical in character and involve any means of recognizing qualitatively or quantitatively the ionization in air or other gases produced by the alpha, beta and gamma rays. There are two instruments which are usually used for such a purpose, namely, an electrometer or an electroscope.

The first instrument is adapted for use in chemical and physical laboratories, and is especially useful where a large number of readings are desired on a radioactive material in a short space of time. For example, where a decay curve is required and the points on the curve involve very short intervals of time, an electrometer is very useful, owing to the fact that the length of time in making a reading on even a not very sensitive product is short, due to the senstiveness of the instrument that may be used. For ordinary practical purposes, however, an electroscope is much more satisfactory, and the use of the electroscope only will be described in detail in this article. A suitable instrument usually consists of two compartments, one above containing a suspended gold or aluminum leaf in front of which is attached a reading microscope, and one below in which the ore, radioactive solid or radioactive gas, to be tested is placed.

If the material is a solid, there is a suitable door to the lower compartment which can be opened and closed for the introduction of the material. If radioactive gas is to be tested, the lower compartment is airtight and has two stopcocks, one for exhausting the chamber, and the other for the introduction of the gas after partial or complete exhaustion. Usually the leaf is electrically charged by means of a piece of vulcanite rubbed on the sleeve of a coat, or by means of a battery of small dry cells, or any other suitable means of getting a sufficiently high voltage; the charge causing the leaf to rise. Then the natural leak of electricity from the leaf is noted on the scale, using a stop-watch to determine the time the leaf drops between two different points, and calculated as a certain number of divisions per minute.

Approximate Method for Solids.—If an approximate determination of the activity of a solid such as an ore is desired, the material is placed in the compartment below and the leak of the leaf noted as before. If the ore contains uranium, radium, or any other radioactive element, the rate at which the leaf falls will always be faster than the natural leak of the instrument itself, owing to the ionization of the air in the chamber by the rays given off from the radioactive material. There are a number of precautions, however, to be taken in making such measurements. First, the illumination during the taking of the readings

should be constant, and, therefore, it is better to have the electroscope in a room artifically illuminated rather than using ordinary daylight which will vary from time to time. Second, readings should always be taken between the same points on the scale. Third, in comparing two ores, their physical condition should be as nearly as possible the same. This may be roughly done by passing them through the same mesh sieve, preferably 40 or 60 mesh. Of course, every particle of the ore must be ground until it finally passes this sieve. The same weight should be taken and the same surface should be exposed in the electroscope.

In order to get these conditions conveniently, it is advisable to use a brass plate about one-quarter inch thick, of a size to fit into the bottom compartment of the electroscope; and in this should be cut by means of a lathe a circular depression one-eighth inch deep and about 3 in. in diameter. This can be done by any brass worker. The bottom and sides of the depression should be perfectly smooth. The ore to be tested is poured into the depression, the plate tapped gently so as to settle the ore, and then by passing the edge of a flat piece of metal across the surface of the plate the extra ore is wiped off and the depression left exactly filled with ore, having a flat surface. In this manner a fairly uniform weight of material is obtained for comparison and the surface exposed in the electroscope is approximately constant. Of course, the density of the ores tested varies, but the method is accurate enough to give approximate results. The plate with the ore is introduced into the bottom compartment of the electroscope and a reading taken. The ore is removed and replaced by a sample of carnotite of known uranium content, which serves as a standard. This sample, of course, is passed through the same mesh sieve as the sample being tested. The relative radioactivities: that is, the rates at which the leaf falls, are roughly proportional to the amount of radioactive elements present.

In the case of an ore, the total activity will be due to the uranium, radium and other disintegration products of the series. In the case of a concentrate, such as radium-barium sulphate, the activity will be due to radium alone. Too much emphasis can not be placed upon the fact that this method is only applicable to comparison between similar radioactive products, and results are only approximate. For example, a carnotite ore must be checked against an analyzed carnotite ore; pitchblende against an analyzed pitchblende ore, and a concentrate against a similar type concentrate. As has already been pointed out, the physical condition of the material affects the results very markedly.

The following example will show how to make a calculation:

METHOD OF CALCULATING PERCENTAGE OF U_3O_8

Natural leak of instrument = 5 divisions in 10 min.
Natural leak of instrument = 0.5 division per min.
Rate of fall of leaf with standard ore (3 per cent U_3O_8) = 48.5 divisions per min.
Rate of fall of leaf with ore to be tested = 36.5 divisions per min.
Subtracting from each of these figures the natural leak, 0.5 divisions per min., we have 48 and 36. The percentage of U_3O_8 in the ore will then be $\frac{36 \times 3}{48} = 2.2$.

If the natural leak is as low as 0.5 division per minute and the radioactivities of the samples are as high as those indicated in the above experiment, the natural leak can be neglected, as the error from it is less than the probable experimental error.

Exact Determinations by Emanation Method.—The exact determination of radium is by means of the emanation method which involves separating radium

emanation as a gas from its parent radium, and measuring its quantity in a gas-tight electroscope previously standardized with a known amount of radium emanation. Analyzed pitchblende has been employed to furnish known quantities of emanation for purposes of standardization. Pitchblende is selected because it is a primary uranium mineral and contains the equilibrium amount of radium to uranium. Therefore, by analyzing the mineral carefully for uranium it is possible to calculate exactly the amount of radium present; and a satisfactory standard is thus readily obtained. Secondary uranium minerals, such as carnotite, autenite, torbernite, etc., do not always contain the equilibrium amount of radium and, therefore, can not be used as a standard.

Three general methods of procedure may be used, as follows: (1) Release and measure the emanation from a substance in which it is in equilibrium with the radium content. This condition will usually not be fulfilled unless the substance has been retained for a month or more in a closed container. In exceptional instances, however, the radium might be contained in a solid of very compact structure, or with a glazed surface, so that no spontaneous loss of emanation could take place. But even with a dense mineral like pitchblende, the leak of emanation, called "emanating power," amounts at ordinary temperature to several per cent.

This circumstance suggests the second procedure. (2) Liberate and measure the emanation retained in the solid and apply as correction the "emanating power," which must be determined separately and preferably after the solid has been in a closed retainer for 1 month. Both of the above procedures, applicable in general to solids only, involve in practice long delays; and, although they are adapted to scientific investigation, they are not suited to radium measurements for the purpose of plant control when quick results are desired. The following procedure is shorter and preferable when its use is possible. (3) Remove the emanation completely from sample of the substance to be analyzed for radium; close it at once in a gastight vessel and allow the emanation to accumulate for a convenient period, such as from 1 to 10 days. Then remove it and measure it, making a time correction to find the maximum amount that would have been formed on the attainment of equilibrium. For removal of emanation the radium must be contained either in solution, or in a state of fusion. When radium and barium are in a solution together, and there is a tendency for partial precipitation, either as a sulphate or as a silicate, the two elements will usually precipitate in the proportion in which they exist in the solution. The presence, therefore, of a moderate amount of barium in solution has a tendency to hold the radium in solution and give more exact results by the emanation method.

Treatment for Solution Containing Barium in Large Excess over Radium.—For a solution containing barium in large excess over radium, the treatment is as follows: Place a suitable portion of the solution—such as will contain about 1×10^{-8} g. of radium—in a small Jena flask and add to it a suitable quantity of 1:1 nitric acid. Add a few glass beads and boil 5 to 10 min. to remove all emanation. Allow slight cooling and then close the flask tightly with a one-hole rubber stopper provided with a glass tube drawn out above to a capillary tip. Seal the tip while some steam is still in the flask, in order to provide a partial vacuum which should be maintained until the flask is again opened, thus affording a proof that no outward leak of gas has taken place. Note the exact time and date of sealing.

The treatment for a solution containing little or no barium is to add a suitable portion of 1:1 nitric acid which is saturated with barium nitrate, and then proceed as in the treatment described above.

Procedure for Liquids Containing Excess of Sulphate or Carbonate.—The detailed procedure for treating a liquid containing an excess of sulphate or carbonate, but no barium, is as follows: An excess of barium salt is added to the liquid, and the precipitate is filtered off. The filtrate containing an excess of barium is made acid with nitric acid to the point of precipitation, and is given the treatment outlined above for a solution containing barium in large excess over radium. The precipitate, if barium sulphate, is fused with four or five times its weight of fusion mixture of sodium and potassium carbonates and is treated as described later for fusions. If the precipitate is barium carbonate, it is dissolved in nitric acid containing sufficient sulphuric acid to precipitate an amount of barium sulphate convenient for fusion, which is filtered off. The filtrate that is obtained may be combined with the original filtrate and given the treatment as described for a solution containing barium in large excess over radium. All radium is then contained either in the filtrate, with excess of barium, or in the barium sulphate precipitate. The latter is fused with sodium carbonate and treated as described in the next section. Both of the liquid fractions are closed simultaneously (within 15 min.) so that the time of accumulation will be the same for both lots of emanation which can be later introduced into one electroscope to determine the total radium.

Fusion Method for Radium Determinations.—If the radium is contained in a substance not readily soluble, such as a radium-barium sulphate, fuse a suitable quantity in a small platinum or porcelain boat with four to five times the weight of sodium or potassium carbonate and note the exact time at which the material becomes solid. Close this boat in a glass tube as shown in Fig. 1. Allow the emanation to accumulate 2 or 3 days. Connect the glass tube at one end to a highly exhausted electroscope and at the other to a stopcock. Break the glass tips inside the rubber connections and exhaust the air from the glass tube into the electroscope several times, leaving enough vacuum in the electroscope chamber to accommodate the gas to be introduced later. Break the glass tube, remove the boat and its contents, wrap in a filter paper and place in the neck of a flask as shown in Fig. 2; it is then ready for treatment with 1:1 nitric acid after the flask has been connected with the gas burette as shown in Fig. 3. In this treatment the flask is tipped until the acid comes in contact with the carbonate fusion, thus beginning a gas evolution. The stopcock is immediately opened to the gas burette above and the boat and contents are then thoroughly wet with acid and jarred down from the neck of the flask to the body of the acid.

As regards larger fusions, the evolution of carbon dioxide may become rapid and care should be taken in handling them; but in small fusions not exceeding 1 g., the boat may be shaken down directly into the acid, which should be heated to boiling as soon as the gas evolution begins to slacken. All of the carbon dioxide is, of course, absorbed by the strong sodium hydroxide solution which is contained in the gas burette. The boiling off from this point is performed as with solutions discussed below.

Boiling off Emanation from Solutions.—For boiling off emanation from solutions, the procedure is as follows: Set up an apparatus as shown in Fig. 3, wiring rubber connections at *a* and *b* to insure tightness. Put into the leveling bulb *c* a stick of sodium hydroxide 2 to 3 in. long, or more if a large quantity of carbon dioxide is to be absorbed; make sure that stopcock *d* is closed and stopcock *e*

open; pour boiling distilled water into the leveling bulb and allow the alkali to go into solution. If the boiling is too violent, put a one-hole stopper lightly into the mouth of the leveling bulb. After the alkali has gone into solution raise the leveling bulb until the gas burette is filled to the stopcock *e*. If the quantity of air to be boiled off is small, some air may at first be left in the gas burette. Close stopcock *e* and lower bulb *c* to its original position. Break the glass tip *f* inside

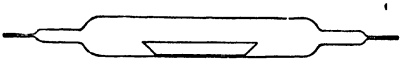


FIG. 1.—Apparatus for fusing Ra-Ba sulphate.

the rubber tubing at *a*, and slowly open *d* to ascertain whether there is vacuum in the flask *g*. If so, close *d* again and begin to heat flask *g* over wire gauze. Test the vacuum every few seconds and as soon as the pressure is outward open

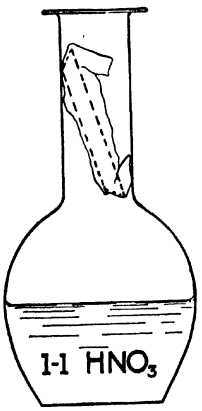


FIG. 2.—Fusion ready for acid treatment.

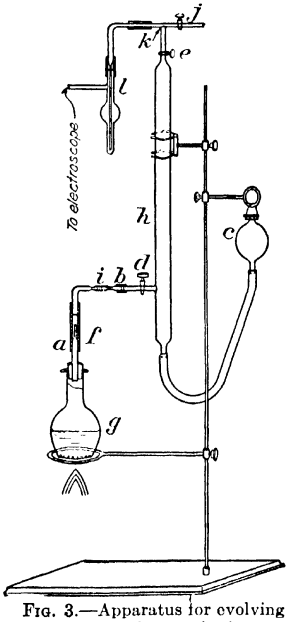


FIG. 3.—Apparatus for evolving emanation and transferring to electroscope.

d, and cause the flask to boil vigorously. Continue boiling until live steam has heated to boiling all the liquid in the gas burette *h*. This boiling should never be less than 5 min., and sometimes 10 to 15 min. boiling is desirable. After the glass tip *f* has been broken the liquid is likely to be carried upward by steam and in some instances has lodged in the stopcock *d* and caused serious explosions. As a precaution, a roll of thin platinum foil can be introduced into the glass tubing, as indicated at *i*, or the stopcock *d* may have a wide bore, which also obviates

the danger mentioned. After the boiling off has been completed, remove the flame, and as soon as the liquid begins to draw back through the stopcock *d* close the stopcock and remove the flask entirely. Evacuate the electroscope chamber to a suitable vacuum, either by means of an aspirator, or more conveniently, a hand pump, and connect the sulphuric acid microdrying bulb *l* to the electroscope and to the gas burette as indicated in Fig. 3. Be sure that stopcock *j* is closed; open first the cock of the electroscope for a moment and reclose it; then slowly open stopcock *e* to full width and then gradually open the stopcock to the electroscope, allowing the gas to bubble through the microdrying bulb at a fairly rapid rate.

When the liquid in the gas burette has risen exactly to the point *k* close stopcock *e* and open stopcock *j*, allowing dry, dust-free air which should preferably be taken from outside the laboratory to sweep out the connections for a few minutes; then close the stopcock to the electroscope, reopen stopcock *e* and allow the liquid in the gas burette to fall back 3 or 4 in. below the shoulder; close *e*, and then pour off all excess liquid out of *c;* close *j* and again open *e* to the electroscope, allowing air to bubble from the bottom of the gas burette *h* through its entire length to insure the removal of any emanation that may have remained dissolved in the liquid. Air should be allowed to bubble into the electroscope chamber until normal pressure has been almost restored. The above procedure for boiling off radium emanation is used for carbonate fusions introduced into acid, and also in handling any solids that are to be dissolved directly. For example, ground pitchblende and carnotite ore may be wrapped in filter paper in the way in which such a fusion is wrapped in Fig. 3, or sealed in small glass bulbs which are opened by being crushed against the bottom of the flask by tapping on the glass stem projecting through a second hole in the rubber stopper.

Construction of an Electroscope.—Figure 4 shows an electroscope which is very suitable for radium determinations by the emanation method. Figure 5 represents a section of this electroscope, showing the gastight chamber at the bottom with openings at *o* for connections with stopcock. The electrode *e* is a brass cylinder ½ in. in diameter. It is suspended by a small brass rod ⅛ in. in diameter, which screws into the top of the electrode, passing upward through the insulating material *d*, and terminating in a small conical top, *c*, serving to make metallic contact with the leaf system above. The leaf system, *f*, is supported from the top of the cylinder where it is held in place by the sealing-wax insulation set in a milled-head cap, *g* which screws into a vertical collar on the cylinder ¼ in. in height. The cap is hollowed out inside to contain the insulating wax, from which a flat brass rod, *f*, ¼ in. broad, about 1/16 in. thick and 2¼ in. long projects downward, terminating below in a light brass spring, *s*, to make contact with the conical top of the electrode of the ionization chamber. The leaf is of aluminum, about 2 in. in length, and is attached to a small offset at the top of the brass rod by a moisture contact. The electroscope can either be charged by means of a piece of hard rubber or, better, by means of a battery of flashlight storage cells giving 500 or 600 volts. The reading microscope in front of the instrument carries a micrometer scale serving to measure the rate of discharge of the leaf. The eye-piece fits firmly into the case so that its rotation is difficult after the micrometer scale has been set parallel to the leaf.

Order of Procedure in Using Electroscope.—(1) Set up electroscope and charge for 15 min. from a battery with just sufficient voltage to hold the leaf on

the part of the scale to be used later. (2) Observe the natural leak during 15 or more minutes. (3) Carry out the calibration control by means of penetrating rays if radium is available for this purpose. (4) Detach the top and evacuate the lower chamber to the desired vacuum. (5) Pass the emanation-air mixture through a sulphuric acid drying tube into the evacuated chamber and restore

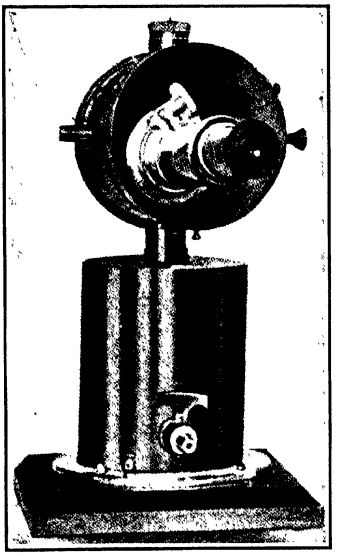


FIG. 4.—Electroscope with interchangeable ionization chamber.

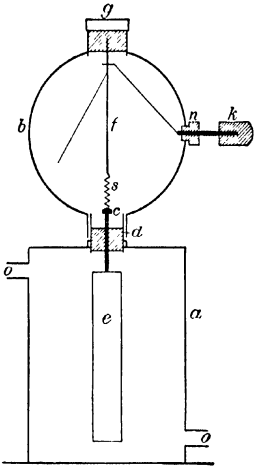


FIG. 5.—Cross-section of electroscope (one-fourth size.)

normal pressure. (6) Allow the emanation to stand in the discharge chamber for 3 hrs. (7) Charge for 15 min. as before. (8) Take three readings if agreements are good, or 10 if deviations are greater than 1 per cent. (9) Clean out the emanation chamber by drawing dry, dust-free air through it for some time (over night if convenient). (10) Calculate the discharge and subtract the natural leak, expressing both in divisions per second. (11) Compare the corrected discharge with the calibration of the instrument to determine the quantity of radium under measurement, taking time corrections into consideration.

Calibration of Electroscope.—The calibration of the electroscope is carried out in exactly the same way as in ordinary measurements, except that a known quantity of emanation is introduced. This known quantity may be obtained in two ways as follows: (1) From a standard solution of some radium salt by passing air through it until its emanation is all transferred into the electroscope. This method is not satisfactory, as it is difficult to know always the amount of radium in solution, owing to the tendency of a portion of the radium to precipitate out of solution as sulphate or silicate. (2) The preferable practice is to use high-grade analyzed pitchblende, a suitable quantity being dissolved for each standardization, and the quantity of radium being calculated from the uranium analysis. The quantity of radium emanation obtained on dissolving the pitch

blende will not correspond exactly to the radium content because a small fraction of from 2 to 10 per cent of the gas diffuses from the ore; this fraction, termed the "emanating power" of the ore in the cold, must be determined by sealing a quantity of the ore in a tube for a month or more, and drawing off the emanation into an electroscope by the passage of air. The "emanating power" thus determined in the standard sample is used as a subtraction correction. Convenient quantities of radium emanation are those that will produce a discharge of the order of one to two scale divisions per second. The use of pitchblende as a standard is based upon the fact that in any unaltered uranium mineral the ratio of the radium present to the radium is constant. One gram of uranium is in radioactive equilibrium with 3.3×10^{-7} g. of radium.

Sample Determination of Radium Content of an Ore.—A sample of pitchblende loses 10 per cent of its emanation at room temperatures. It contains 50 per cent metallic uranium. Therefore 22 mg. of the ore will, on dissolving in acid, liberate emanation in equilibrium with 10 mg. (0.01 g.) or metallic uranium. This emanation, 3 hr. after introduction into the electroscope, causes the leaf to fall at the rate of 40.5 divisions per minute. The natural leak (0.5 divisions per minute) subtracted from this leaves 40 divisions per minute due to the emanation. Therefore the fall of one division per minute represents the total emanation associated with $\frac{0.01}{40} = 2.5 \times 10^{-4}$ g. of uranium in the mineral. This is the "constant" for the electroscope. One gram of ore is fused with fusion mixture as already described. At the end of a month the emanation obtained from the two solutions is introduced into the electroscope. After 3 hr. the rate of fall of the leaf is 18.5 divisions per minute. Subtracting the natural leak (0.5) leaves 18 divisions per minute. Therefore 1 g. of the ore contains $18 \times 2.5 \times 10^{-4} = 45 \times 10^{-4}$ g. of uranium.[1] As 1 g. of uranium is in radioactive equilibrium with 3.3×10^{-7} g. of radium, 1 g. of the mineral will contain $(45 \times 10^{-4}) \times (3.3 \times 10^{-7}) = 1.48 \times 10^{-9}$ g. of radium.

OTHER RADIOACTIVE ELEMENTS

Mesothorium.—Of the other radioactive elements which have commercial use mesothorium is the most important. As is seen from Table 2, it is a disintegration product of thorium and is, therefore, associated with this metal in all thorium minerals. Its half-life period is very short, compared to that of radium; being only 5.5 years. Therefore, commercially it has not the same value as radium, especially for cancer treatment or for purposes where it would naturally be carefully preserved and a long life would be of advantage. When its commercial use is likely to last over a limited period, such as in luminous paint for cheap watch dials, electric push buttons, etc., it is just as useful as radium and can be substituted for the latter element in luminous paint for such purposes. Owing to the fact that mesothorium 1 gives off beta rays only, and the alpha rays

[1] This is true only when the uranium and radium are in equilibrium. In other cases it represents the theoretical amount of uranium in equilibrium with the radium actually present. In pitchblende, since it is a primary mineral, the ratio of uranium to radium is constant, 1 g uranium = 3.3×10^{-7} g. of radium, or 2,000 lb. U_3O_8 = 331 mg $RaCl_2$, and if the percentage of uranium is known by analysis, the amount of radium present can be calculated directly. In carnotite and other recent uranium minerals, the equilibrium ratio is not constant and the radium present has to be found by experment.

are the main source of luminosity in paints used for watch dials, etc., it is necessary for the mesothorium 1 after preparation to be allowed to "ripen" for a year or even 2 years so that the alpha rays, due to the gradual accumulation of radiothorium, can be used. The general effect, therefore, is for the luminosity of such paints gradually to increase for 2 or 3 years and then, after coming to a maximum, gradually to decrease. Mesothorium 1 chemically is allied to barium and radium and, therefore, can be precipitated with barium just as radium is. The usual procedure in manufacture is to add 2 or 3 lbs. of barium chloride per ton of monazite treated. When the monazite is heated with sulphuric acid in order to extract the thorium and other rare earths, the barium sulphate and mesothorium sulphate are left behind in the residue and can be recovered from the coarse silica, etc., by sliming. The crude concentrates so obtained can be still further purified by fusion with a mixture of caustic soda and sodium carbonate, by which means the silica is converted into sodium silicate and can be washed away from the barium-mesothorium carbonates, or the silica can be eliminated by the use of hydrofluoric acid. The refined sulphate so obtained is purified by the same methods described under the refining and purification of radium.

Actinium.—Actinium was discovered by Debierne in the iron group separated from pitchblende, very shortly after the discovery of radium and polonium. Actinium itself is probably rayless, but its first product, radioactinium, has a half-life period of 18.8 days. Actinium preparations when first made increase enormously in activity over a period of several months. It is, therefore, comparatively easy to overlook its presence, unless the preparations are kept and their activity tested periodically. Actinium is easily obtained with iron and rare earths by precipitating barium as sulphate in an acid solution; and this accounts for its presence in pitchblende residues. In working these up, the acid solutions, after removal of polonium by means of hydrogen sulphide, are oxidized and precipitated with ammonia; the actinium being precipitated and the radium and barium, of course, remaining in solution. The precipitate may be extracted with dilute hydrofluoric acid; the insoluble part consisting of La, Di, Ce and Th retaining most of the actinium. The rare-earth element most closely associated with actinium is lanthanum. In the presence of ammonium salts the precipitation of actinium is far from complete, but it is completely precipitated in the presence of manganese from basic solutions.

Polonium.—(Radium F). Polonium is one of the short-lived radioelements, having a half-life of 140 days and giving off alpha rays only. It was discovered owing to the fact that it is closely allied to bismuth and precipitates with bismuth in the second group. For this reason it is easily separated from radioactive minerals in crude form by digesting radium containing residues of pitchblende or carnotite ore itself with hydrochloric acid. A part of the polonium is dissolved and may be precipitated with hydrogen sulphide. The polonium may be purified: (1) By fractional precipitation from solutions made very acid with hydrochloric acid, the polonium being enriched in the precipitate. (2) By fractional precipitation of the basic nitrate with water, the precipitate being enriched. (3) By sublimation in vacuo, the polonium being more volatile. By immersing a plate of bismuth, silver, copper, etc. in a hydrochloric acid solution, the polonium is practically completely precipitated. The theoretical quantity

of polonium in minerals is 1 g. for 14 tons of uranium element, assuming that no radium emanation escapes from the mineral. As such a condition never exists in nature, the actual amount is less then the theoretical.

Radiolead.—(Radium D). As has been previously stated, there are three kinds of lead: One representing the final disintegration product of the uranium series; one the final disintegration product of the thorium series; and ordinary lead which so far as we know does not owe its origin to radioactive changes. The first has an atomic weight of 206, the second 208, and ordinary lead 207. Since radiolead, or radium D, resembles lead perfectly in all of its chemical reactions, in the treatment of uranium minerals it can not be separated from the lead which is found in such minerals. It is, therefore, obtained in association with this lead when the latter is precipitated during the refining of the radium-barium sulphate. Common commercial lead contains traces of radium D and is more distinctly radioactive than most other metals. For this reason, in making instruments, a very old lead should if possible be employed, as in this the radioactive constituents will largely have decayed. Another source of radium D is old radium, in which the radiolead has to a certain extent accumulated. If, however, a sample of this element is required in concentrated form, the best method is to remove the emanation periodically from a radium solution kept in an airtight vessel and introduce the emanation into a closed vessel. As the emanation decays the radiolead will be formed and will be deposited on the sides of the vessel. This can then be dissolved by acid and precipitated by ammonia or other lead precipitants, provided there is a small amount of lead salt introduced in order to give a precipitate sufficiently large to be handled.

SECTION XXVII

RARE METALS

By Richard B. Moore[1]

Introduction.—It is not possible within the scope of the present volume to give even an outline of the chemistry and metallurgy of all the rare metals. A selection, therefore, has been made of those which are of most importance in the industries, and the present article will deal only with the following: Vanadium, uranium, tungsten, molybdenum and thorium.

VANADIUM

(Atomic Weight = 51.0)

Occurrence.—Vanadium is never found free in nature. Its ores are fairly widely distributed, but seldom occur in quantity in any one locality. The principal ores are patronite, roscoelite, carnotite, vanadinite, cuprodescloizite, zinc descloizite, mottramite and pucherite. Vanadium is found in small quantities in certain iron ores, and in the ash from lignites, coals and other carbonaceous materials.

Patronite is an impure vanadium sulphide found in Minasragra, Peru. The composition is approximately V_2S_9, and it is associated to a certain extent with carbonaceous material, pyrites and free sulphur. The area in which the ore lies[2] is along the western limit of a broad anticline in "Jura-trias" and Cretaceous rocks. A section shows the series in this locality to be composed of green shales, thin beds of limestone and red shales. Vanadium is found only in the red shales. The deposit proper appears to be a lens-shaped mass, 28 ft. wide and 350 ft. long. The mineral that constitutes the larger portion of the deposit has been called "Quisqueite." It is a black carbonaceous substance containing sulphur, with a hardness of 2.5 and a specific gravity of 1.75. There is also a lesser quantity of a coke-like material with a hardness of 4.5 and a specific gravity of 2.2. Neither of these contain vanadium. The vanadium is mostly in the southern end of the ore body, and to a depth of 20 ft. is largely in the form of a red calcium vanadate, and carries as much as 50 per cent vanadic oxide. It occurs in pockets and fills the cracks and fissures in a fine shale.

Below this shale is the mother lode. It is from 9 to 30 ft. thick and extends along the greater length of the deposit. It carries as high as 10 per cent vanadic oxide and nearly as much sulphur. On the east and south sides below the mother lode is found a hard blue-black vanadium shale carrying as much as 13 per cent vanadic oxide and 4 to 5 per cent sulphur. Patronite, the main vanadium mineral, is greenish-black and has a hardness of 2.5 and a specific gravity of 2.71. It contains from 19 to 24.8 per cent vanadic oxide and sometimes 50 per cent of combined sulphur. This deposit in Peru constitutes the largest known source of vanadium at the present time and

[1] Chief chemist, Bureau of Mines, Washington, D. C.

[2] D. F. Hewett, *Eng. and Min. Jour.*, Vol. **82**, Sept. 1, 1906, p. 385; W. F. Hillebrand, *Jour. Am. Chem. Soc.*, Vol. **29**, 1907, p. 1019.

furnishes the American Vanadium Company of Pittsburgh, Pa., with practically its only supply of ore. As this company has been the largest producer of ferrovanadium and vanadium compounds in the world, patronite is by far the most important ore of vanadium from the commercial standpoint.

Roscoelite, or vanadium mica, is the second most important vanadium mineral commercially. It has a somewhat indefinite composition; the formula $H_8K_2(MgFe)$-$(AlV)_4(SiO_3)_{12}$ representing its composition fairly well. It exists in minute scales of a brown to greenish-brown color. Sometimes the color is actually green. The specific gravity is 2.92 to 2.94. It exists rather widely distributed in nature, but at only one place in the United States is it worked commercially, namely, near Newmire, San Miguel County, Colo.

Carnotite is mainly of importance on account of its uranium and radium content, but also carries usually from 3 to 5 per cent V_2O_5 in ordinary commercial ores. It is found mainly in Southwestern Colorado and Eastern Utah, but also exists in smaller quantities in other localities, such as South Australia, Portugal, etc. It is a potassium uranyl vanadate of the following approximate composition $K_2O.2UO_3.V_2O_5.3H_2O$. The crystals are canary-yellow in color and usually exist as incrustations on other minerals, or are disseminated through a sandstone in which they are usually found. It also contains small traces of calcium and barium.

Vanadinite, or lead vanadate, is widely distributed, especially in certain of the western states of the United States, particularly Arizona, New Mexico, Nevada and California. The largest deposits are in Arizona, where it is frequently associated with wulfenite, or lead molybdate. The deposits are almost always low-grade and for this reason this mineral has not been used to any great extent as a source of vanadium in the United States. In Mexico the vanadinite occurs at Villarosales, Chihuahua. In Spain important deposits of vanadinite occur near Santa Marta, Estramaduras. The ore is found in a sandstone which contains on an average 3 per cent vanadic oxide. This can be concentrated, and these deposits supplied most of the vanadium used in the world up to the opening of the Peruvian mines. The mineral occurs in prismatic hexagonal crystals, and has a specific gravity of 6.6 to 7.1. It varies in color from ruby-red to yellowish and even brown.

Cuprodescloizite is a hydrated lead-copper vanadate of the probable compositino $(PbCu)_2(OH)VO_4$. Commercial samples of the ore may carry as much as 23 per cent PbO, 7 per cent CuO and 8 to 10 per cent V_2O_5. The largest deposit of this mineral known at the present time is in the Shattuck mine at Bisbee, Arizona, although it is found in a few other localities in the United States.

Zinc descloizite is a mineral very similar to cuprodescloizite, where the zinc replaces the copper. It is found in Nevada, especially around Goodsprings, in New Mexico, Arizona and in Argentina. Mottramite, a vanadate of lead and copper, and pucherite, a bismuth vanadate, are of lesser importance to the minerals already described.

Extraction from the Ores.—The method of extraction which can be used for vanadium ores varies materially with the ore and its grade. In general, a different metallurgical process must be used for every mineral treated, although there are, of course, some general similarities between the methods used.

Patronite is treated by first roasting in order to eliminate the sulphur as far as possible. It can then be leached with either sulphuric acid, filtered and the filtrate evaporated to a crude vanadic oxide, or the roasted ore can be leached with alkali—sodium carbonate or caustic soda, which will dissolve the vanadium as sodium vanadate. From this a high-grade vanadic oxide can be obtained by acidifying with sulphuric acid, or after neutralization the vanadium can be precipitated as vanadate of iron by means of ferrous sulphate.

Roscoelite is treated commercially at only one place in the United States, namely, at Newmire, Colo., where the Primos Chemical Co. has a mill. The method they use is to roast the ground ore with salt and a small percentage of ground pyrites. The ore contains almost no uranium, and no attempt is made to recover the minute quantity found in some of it. The mixed ore, salt and pyrites are coarsely ground and run into a dryer which reduces the moisture to 1 per cent. The material which comes out somewhat caked is ground to 20 mesh and roasted in a furnace for about 3 hr. The roasted material is delivered at the bottom of the furnace to conveyors which carry it to lixiviation tanks where it is treated with water and filtered. The vanadium is now in solution as sodium vanadate. A solution of ferrous sulphate is added, and the vanadium is precipitated as vanadate of iron. This precipitate is filtered out of the solution and partially dried and shipped to the company's reduction works at Primos, Pa. Roscoelite is not very amenable to acid-leaching methods as the mineral is quite insoluble. G. A. Koenig (U. S. Pat. 986,180) claims, however, that the mineral can be decomposed by either dilute sulphuric acid or hydrochloric acid under proper treatment as regards both heat and pressure. In practice, he proposes to use a solution containing 20 per cent sulphuric, hydrochloric or other acid at a temperature of about 200°C. and under a pressure of 225 lb. per square inch; and he claims that this process will completely decompose and dissolve the roscoelite within a few hours.

Carnotite is almost exclusively treated for its radium content, and practically all metallurgical processes for the treatment of carnotite have in view the extraction of the radium primarily, while the recovery of the uranium and vanadium is of secondary importance. Some processes, therefore, do not obtain a high recovery of the vanadium. Metallurgical methods for the treatment of carnotite are discussed more fully in the article on "Radium" in this volume, and under "Uranium" in this section. In order to extract vanadium from carnotite, all that is necessary is to follow the process originally patented by Haynes and Engle (U. S. Pat. 808,839). The ore is first crushed to 12 mesh and is then boiled with a solution of an alkaline carbonate, preferably sodium carbonate, until the uranium and vanadium are dissolved. The strength of the sodium-carbonate solution and the time necessary to boil are determined by the proportion of uranium and vanadium in the ore, and will vary considerably. After these materials are dissolved, the clear solution is treated in a separate tank, where the uranium is precipitated as sodium uranate by the addition of sodium hydroxide to the solution. This precipitate is then filtered from the solution which contains the vanadium. The vanadium can be precipitated on neutralization as iron vanadate or calcium vanadate.

Vanadinite was originally treated by leaching with sulphuric acid. This dissolved the vanadium and left the lead as insoluble lead sulphate, from which the lead could be recovered by smelting. The process was not a success, because the action stopped after a short time, owing to the crystals of the vanadinite being coated with the lead sulphate, which prevented further action. J. E. Conley has thoroughly studied the treatment of vanadinite.[1] The method recommended by him is to fuse the vanadinite concentrate with a mixture of soda ash and caustic soda, which gives a better melt and a better recovery than soda ash alone. The lead is recovered as metallic lead and the vanadium is precipitated by means of slaked lime, giving calcium vanadate as a product. If any trace of molybdenum is present, the latter metal does not come down with the vanadium and is thus eliminated. The calcium vanadate can be treated with sulphuric acid, the precipitated calcium sulphate filtered off, and the vanadium recovered as high-grade vanadic oxide.

Cuprodescloizite has never been treated commercially but, as it constitutes an important and potentially fairly large source of vanadium, the method of Conley[2] is

[1] *Chem. and Met. Eng.*, Vol. **20**, No. 10, p 514.
[2] *Chem. and Met. Eng.*, Vol. **20**, No. 9, p. 465.

of interest. The object is to recover the lead, copper and vanadium. Conley found that a sulphuric-acid leach gives a fairly satisfactory extraction, but his preferable method is to subject the ore to a preliminary fusion with nitre cake, followed by a hot-water leach, and then treating the residue with sulphuric acid. By heating the ore with an equal weight of nitre cake, approximately two-thirds of the ore can be decomposed and the corresponding values extracted. The remaining values are then extracted by leaching the residue with about one-half as much acid as is required in a straight-acid treatment.

Zinc descloizite up to the present time has not been treated commercially, and no methods have been published or suggested for its treatment. The principal deposits in Nevada carry considerable quantities of calcite, which make an acid treatment expensive and, therefore, undesirable.

Concentration Methods.—Most vanadium ores are not readily amenable to concentration. Patronite is partially concentrated by roasting the sulphide to the oxide. Cuprodescloizite has not been concentrated commercially, and the same can be said of zinc descloizite. It is probable that a partial concentration could be made in both cases by screening or by sliming, but the recoveries are not satisfactory. Roscoelite is not concentrated by the Primos Chemical Co., the ore being treated direct. The writer, however, knows of one gold ore in California, which contains roscoelite, and from which a high-grade vanadium concentrate is obtained during the regular concentration of the ore for gold. This, however, is exceptional. Vanadinite is the only vanadium ore which can readily be concentrated, and this is done by the usual methods involving tables and slimers. It is, however, difficult to separate vanadinite from wulfenite, a mineral with which it is frequently associated, owing to the fact that both minerals have almost the same specific gravity.

Vanadium Compounds.—The compounds of vanadium which are met with commercially are the oxides and the vanadates. The principal oxides are vanadium trioxide (V_2O_3), vanadium dioxide (V_2O_4) and vanadium pentoxide or vanadic anhydride (V_2O_5). The latter is the one which is mainly of interest commercially. It is usually prepared from a solution of sodium vanadate by adding either sulphuric or nitric acid to the solution until slightly acid. In a concentration containing 10 g. of V_2O_5, as sodium vanadate, per liter, if sulphuric acid is added until the acidity is $1/20N$, 92 per cent of the vanadium present can be recovered as pentoxide under favorable conditions. Some vanadium always remains in the filtrate, and if the concentration and acid strength are not favorable, a very considerable amount may remain unprecipitated. There are five sodium vanadates, namely, sodium metavanadate ($NaVO_3$), sodium orthovanadate (Na_3VO_4), sodium pyrovanadate ($Na_4V_2O_7$), sodium tetravanadate ($Na_3HV_6O_{17}$) and sodium hexavanadate ($Na_2H_2V_6O_{17}$). The first three are the important ones commercially. In solution the metavanadates are the most stable, and the orthovanadates the least stable. At a high temperature the reverse is true, the orthovanadates being the most stable, and are formed when vanadium pentoxide is fused with an alkali carbonate, while the meta salt is produced when a solution of alkali carbonate is boiled with vanadium pentoxide. When ferrous sulphate is added to a solution of soluble vanadate, an iron vanadate is precipitated. In commercial practice, the color of the iron vanadate produced varies very materially from dark-brown to yellow, depending upon the conditions

of the precipitation, and may contain from 20 to 45 per cent V_2O_5. The precipitate may consist of mixtures of the iron vanadates in different proportions, and is frequently contaminated by ferric hydroxide.

Metallic Vanadium.—Metallic vanadium has been produced by Gin[1] by the electrolysis of a solution of vanadium trioxide in fused calcium vanadate. The material may also be prepared by the alumino-thermic method, and by reducing the dichloride in hydrogen, in which case the metal is a light whitish-gray colored powder. The metal has a hardness greater than that of steel or quartz. It takes a good polish and is not affected by air. If the powdered metal is thrown into a flame, or rapidly heated in oxygen, it burns brilliantly. Its specific gravity at 15° is 5.5.

Ferrovanadium.—As the principal use of vanadium is in steel and as the vanadium is always added to the steel in the form of ferrovanadium, the manufacture of the latter product is of great importance. Probably 75 per cent of the ferrovanadium produced in this country is made in the open-hearth or crucible furnace by a modification of the thermit process, using aluminum as reducing agent.[2] The remainder is produced by the electric furnace, using 90 per cent silicon as the reducing agent. A satisfactory ferrovanadium for commercial purposes contains from 30 to 40 per cent vanadium and not more than 0.5 per cent carbon, 1 per cent silicon, 2 per cent aluminum, 0.1 per cent sulphur and 0.1 per cent phosphorus. It has a good fracture, is not crystalline and is bright gray in color. Too much carbon is injurious, owing to the fact that it makes a carbide with the vanadium, which is not satisfactory in steel making. In the aluminothermic or Goldschmidt method, vanadium oxide or iron vanadate is reduced with aluminum shot in a gas-fired open-hearth furnace, slagging off the alumina by addition of soda ash or fluorspar. When the oxide is used, iron turnings must also be added. The process is partly exothermic, but not enough heat is generated to carry the reduction to completeness without the application of external heat. The use of iron vanadate requires more aluminum than the oxide, as the iron must be reduced also. In the electric-furnace method, carbon is not a satisfactory reducing agent, and in addition it has a tendency to form carbides which are not acceptable to steel manufacturers. Silicon works excellently and is usually used. The raw materials required are steel turnings, vanadium oxide, silicon, lime and fluorspar. If iron vanadate is used, the steel turnings can be eliminated. While 90 per cent silicon material ground to 60 mesh is preferable, ferrosilicon can be used if necessary. All material should be low in phosphorus, but the presence of sulphur is not so objectionable, as the sulphur content can readily be reduced by re-melting the ferro; the sulphur going into the slag. The melting point of ferrovanadium, practically free from other elements and containing 40 per cent vanadium, is about 1,480°C. The melting point becomes gradually lower as the amount of vanadium is decreased until 35 per cent is reached, when it melts at 1,425°C., and remains stationary until the alloy contains 30 per cent. At this point the melting point gradually rises to about 1,450°C.

Uses of Vanadium.—The chief use of vanadium is for making vanadium steel. The general effect of this rare element on steel is to increase the elastic limit and tensile strength without reducing the ductility. It is usually alloyed with

[1] *Electrochem and Met. Ind*, 1909, No 7, p. 264.

[2] *Bull.* A. I. M. E., August, 1919, p. 1342

chromium or manganese to give chromium-vanadium or manganese-vanadium steel, and is also used in open-hearth and high-speed tool steels. Vanadium is found in much of the steel used in motor cars, locomotive axles, rock drills, etc. The metal causes oxides and nitrides present to pass into the slag, and a certain portion of it also goes into solid solution, rendering the metal more coherent and less liable to disintegration. The quantity of vanadium added to steel is small; the amount usually being between 0.1 and 0.4 per cent.

Other uses for vanadium are as alloys with copper and aluminum. These alloys make excellent castings. It has been used in photography for toning silver-bromide plates to a green color. Vanadium salts have also been used in pottery and glass, and as mordants.

Analytical Methods for Vanadium.—Vanadium in an ore can be recognized qualitatively in the following manner: The ore is ground and boiled with hydrochloric acid, filtered, and to the cold acid solution hydrogen peroxide is added. A deep-red color indicates the presence of vanadium. In the case of a mineral such as roscoelite which is with difficulty soluble in hydrochloric acid, the ore should be fused with sodium carbonate, leached with water, filtered, and the filtrate made acid with hydrochloric acid. On adding hydrogen peroxide, the red color will then be obtained. The choice of a quantitative method will depend upon the ore, or vanadium compound, to be analyzed. Full analytical details are given in U. S. Bureau of Mines *Bulletin* No. 70. The following method is quick and applicable to a large variety of vanadium ores, especially those which contain little insoluble material and are decomposed by acids. Weigh out 1 g. sample of the pulverized ore and add 25 c.c. of concentrated hydrochloric acid. Heat on a hot plate to a small volume, then add 10 c.c. of concentrated nitric acid and continue heating until decomposition is complete. Remove from the hot plate, cool and dilute to about 25 c.c. Now add 10 c.c. of concentrated sulphuric acid and heat to copious fumes. Cool and dilute to 25 to 30 c.c., warm sufficiently to dissolve any ferric sulphate which may have settled out, and then add either sufficient powdered potassium permanganate, or a solution of potassium permanganate (10 g. per liter) to produce a strong permanent pink. Now add 50 c.c. of concentrated hydrochloric and evaporate on a hot plate to fumes of sulphur trioxide. Cool and dilute to about 150 c.c., warm to dissolve the ferric sulphate, and then titrate at 70 or 80° with $N/20$ $KMnO_4$ to a pink which persists for half a minute. It is advisable to run a blank determination, which usually requires from 0.4 to 0.5 c.c. of $N/20$ $KMnO_4$. Fe factor $\times$ 1.63 = V_2O_5. In the case of an insoluble mineral, such as roscoelite, it is advisable to filter off the insoluble material and to treat with hydrofluoric and sulphuric acids in the usual manner to eliminate the silica, and then to redissolve in a mixture of hydrochloric and nitric acids. The method is applicable in the presence of large amounts of iron; molybdenum does not interfere; and arsenic, if present only in small amount, may be overlooked. Large amounts of arsenic, however, should be removed by first passing sulphur dioxide through the solution after evaporating the first time to sulphur trioxide fumes, boiling off excess and passing in hydrogen sulphide. Chromium interferes, but is seldom met in vanadium ores.

URANIUM

(Atomic weight—238.2)

Occurrence.—The principal ores carrying uranium are pitchblende, carnotite, autunite and torbernite. Pitchblende is an impure uranium oxide with rare earths, carrying traces of lead, calcium, iron, bismuth, manganese, copper, silica and aluminum. The specific gravity varies from 6.4 to 9.7, and the hardness is usually about 5.5. Carnotite is described under "Vanadium." Autunite is a hydrated uranium-calcium phosphate, with the formula $Ca(UO_2)_2(PO_4)_2.8H_2O$. It is a bright-yellow mineral usually crystallizing in orthorhombic plates, and has a specific gravity of from 3.5 to 3.9. Torbernite is a copper-uranium phosphate with the formula $Cu(UO_2)_2.P_2O_8.8H_2O$. The crystals are tetragonal with a pearly lustre and of an emerald-green color. The specific gravity is 3.4 to 3.6. A further description of uranium minerals and their distribution can be found under the chapter on "Radium."

Extraction from the Ores.—All uranium minerals carry radium. The amount of radium is usually proportional to the amount of uranium present, although this is not always the case. In primary minerals the equilibrium amount of radium is present, but in secondary minerals such as autunite and torbernite the proportion of radium to uranium varies and is often as low as 60 or even 50 per cent of the equilibrium amount. Notwithstanding this fact, uranium minerals are now always treated for their radium content and not for the uranium; the recovery of the latter being of secondary importance. Consequently, the metallurgy of uranium is really the metallurgy of radium, and full details concerning the treatment of uranium ores will be found under the chapter on "Radium." In order to obtain the uranium alone, practically the same methods that are used for the extraction of radium can be used, the only difference lying in the fact that the radium need not be precipitated as a radium-barium sulphate, this step being omitted. Any method that gives a good extraction of the radium may be used to recover uranium, as it is necessary, of course, to decompose the mineral thoroughly in order to get the radium.

For analytical purposes uranium can be extracted from one of its ores by fusing with excess of sodium carbonate. The melt is broken up, boiled with water and filtered. The uranium goes into solution as the double carbonate of sodium and uranium, and will contain only small traces of aluminum and iron. On the addition of caustic soda in excess, followed by boiling, the uranium is precipitated as sodium uranate. If an ore is treated which also carries vanadium, the latter element will also be found in solution with the uranium. On the addition of caustic soda, the uranium is precipitated, as already stated, and the vanadium remains in the filtrate. It is practically impossible, however, in such a case to precipitate the uranium free from vanadium. Commercially, the precipitate nearly always carries from 5 to 8 per cent V_2O_5. The formula of sodium uranate is $Na_2U_2O_7$, and it usually possesses 6 molecules of water of crystallization.

Concentration Methods.—Most uranium minerals can be concentrated mechanically. This is largely due to the fact that the specific gravity of these minerals is high, particularly pitchblende. Pitchblende can be concentrated by the use of jigs, tables and slimers. On the table it appears as a black streak

representing the heaviest mineral present. Next to this is pyrite, and usually a portion of the pitchblende is found in the pyrite, which constitutes a middling which must either be reground and retreated, or handled chemically. As the crystals of carnotite are extremely small, this mineral is not amenable to ordinary concentration methods. It can, however, be concentrated in two ways: (1) By dry methods; and, (2) by sliming. The most satisfactory dry method involves the use of the ordinary Raymond pulverizing machine with tubular dust collector. This has a beater chamber containing two sets of rapidly revolving beaters. Over the chamber is a cone of galvanized iron, within which is an inner cone provided at its lower end with a swinging discharge gate. The two cones are connected at their upper ends by a number of small gate shutters and have a common top or cover plate. A large pipe from the center of the top leads to an exhaust fan, mounted on the same shaft as the beaters. This fan discharges into a cyclone dust and air separator which is connected by a return pipe with the beater chamber of the pulverizer. A small pipe leads from this return pipe to a tubular dust collector. The Raymond mill is used extensively to pulverize cement, paints, etc. In the sliming method the ore is ground and then stirred in water, getting as much attrition as possible in order to remove the carnotite crystals from the silica grains. The latter settle quickly, and the carnotite with other fine material is slimed off into another vat and allowed to settle. Undoubtedly torbernite and autunite could be concentrated in the same way as carnotite, but up to the present this has not been commercially carried out.

Uranium Compounds.—There are two well defined oxides, namely, UO_2 and UO_3, and these combine to form intermediate oxides, such as U_3O_8. The dioxide is basic and gives rise to uranous salts, the metal being tetravalent. The trioxide is an acid-forming oxide yielding salts known as the uranates, corresponding to tungstates, chromates, etc. Uranium trioxide also gives a number of derivatives in which only one of the three oxygen atoms is replaced by negative groups, and these salts may be regarded as derivatives of the divalent compound radical, uranyl (UO_2). UO_2 is formed by the reduction of U_3O_8 by means of hydrogen. It can be made directly from sodium uranate ($Na_2U_2O_7$) by the method of Parsons, which consists in fusing the oxide with salt containing a little carbon. The fused product is leached and washed; everything being in solution except the UO_2. UO_3 can be obtained by heating uranyl nitrate to 250°C., out of contact with air, the oxide being left behind as a brownish-yellow powder. U_3O_8 may be formed by Wöhler's method. The solution of the uranium ore in dilute sulphuric acid is treated with hydrogen sulphide to remove arsenic, antimony, lead, bismuth, etc.; filtered, and after the addition of nitric acid to oxidize the iron, excess of ammonia is added. The precipitate consists of iron hydroxide and ammonium uranate, and is digested with a strong solution of ammonium carbonate with excess of ammonia in order to dissolve the ammonium uranate. After filtering the liquid, it is allowed to cool, and ammonium uranyl carbonate crystallized out. On igniting this, U_3O_8 is left behind. The alkali uranates are obtained by precipitating a uranic salt with an alkali. The uranates generally have the composition $M_2O.2UO_2$, and correspond to the dichromates. They are yellow, insoluble in water, but soluble in acids. The two principal uranates from the commercial standpoint are sodium diuranate, $Na_2U_2O_7$, and ammonium uranate $(NH_4)_2U_2O_7$. The sodium salt is known as uranium yellow,

or yellow oxide. The hydrated salt contains six molecules of water of crystallization. The color of the sodium salt varies from a dark-yellow to a very bright-canary-yellow. The color is dependent upon the conditions of precipitation, and also upon the presence of excess of alkali. Ammonium uranate is also yellow and has the formula $(NH_4)_2U_2O_7$. On heating to redness, it yields pure U_3O_8.

Metallic Uranium.—Metallic uranium was first prepared in the electric furnace by Moissan.[1] He used 300 parts of U_3O_8 and 40 parts of sugar charcoal and reduced the mixture in a carbon tube in the electric furnace. The crude product contained carbon and was purified by heating in a crucible, brasqued with U_3O_8. This crucible was imbedded in another brasqued with titanium, the object being to prevent action of nitrogen on the reduced uranium. The metal may also be prepared by the electrolysis of the fused double chloride of uranium and sodium in an inert atmosphere, using carbon electrodes.[2] Keeney[3] has prepared the metal by reducing U_3O_8 with carbon in a Siemen's furnace with magnesite walls and carbon bottom. The metal was allowed to cool in the furnace. He got a product containing 88 per cent uranium, 3.67 per cent carbon, and 2 47 per cent silicon, which really consisted of uranium metal and uranium carbide.

Ferrouranium.—Many unsuccessful attempts were made to produce ferrouranium before success was finally achieved. The main difficulty met with was that a low-carbon alloy could not be made by variation of the carbon in the charge because there was such a low recovery of uranium, both when the amount of carbon charged was about the theoretical amount required, and when the carbon in the ferrouranium was low. Carbon could not be removed from an alloy containing more than the allowable amount by using either iron oxide or uranium oxide as can be done in the case of other ferro-alloys high in carbon. When this was attempted the uranium in the alloy oxidized and went into the slag leaving pig iron in the furnace. Keeney[4] was unable to get a ferrouranium containing as much as 30 per cent uranium, and in addition the carbon content was too high. He was, however, able to get a commercially high-grade uranium metal as described above. Gillett and Mack[5] succeeded in making a satisfactory ferrouranium by using a pure UO_2, a low ash coke and a pure iron as raw materials, with calcium fluoride as slag former. They stated that by using a tilting direct-arc type furnace with water-cooled magnesite hearth and sides, it should be possible to produce commercially without a second refining operation ferrouranium of any desired uranium content, say 40 to 70 per cent, with carbon averaging below 2 per cent, silicon below 0 75 per cent, vanadium below 0 5 per cent, and with aluminum, sulphur, phosphorus and manganese all so low as to be negligible.

Uses of Uranium.—Besides its use in steel, uranium has been used for many years as a coloring agent for glass. Sodium uranate is usually desired, although uranium oxide is sometimes used as a substitute. The color produced is opalescent yellow, turning green by reflected light. Usually about 20 per cent of uranium calculated as oxide is required to produce the color; this making the glass quite expensive. Uranium salts are also used in the ceramic industry. It produces yellow, orange and black glazes. The coloring power is great and

[1] *Compt rend*, 1893, Vol **116**, p. 347.
[2] Moissan, *Compt. rend.*, 1896, Vol. **122**, p. 1088.
[3] *Bull.* A. I. M. E., August, 1918, 1354.
[4] *Bull.* A. I. M. E., August, 1918, p. 1353
[5] *Jour. Ind. Eng. Chem.*, Vol. **9**, p. 342, 1917; U. S. Bur. Mines. *Tech Paper* 177.

only small quantities are required. Uranium salts have also been used to some extent as mordants for silk and wool, and also a catalyst in the synthesis of ammonia from nitrogen and hydrogen.[1] In photography, uranium nitrate has been used as a sensitizing agent for paper. With potassium sulphocyanide it can be used for toning bromide prints.

Since Keeney and Gillett made ferrouranium and commercial uranium metal, a considerable amount of interest has developed in connection with uranium steel. One firm in this country has had ferrouranium on sale for some time and has been coöperating with one or two steel manufacturers in the manufacture of uranium steel. One part of uranium is supposed to replace from 2 to 3 parts of tungsten in high-speed steels. Keeney[2] states that ferrouranium can be added to steel in quantities up to 4 per cent with a uranium recovery of at least 50 per cent; and a recovery of 70 per cent can be made in steel containing less than 2 per cent uranium. A considerable portion of the carbon and silicon in the ferrouranium seems to enter the steel. For a steel containing less than 2 per cent uranium, the ferrouranium can be added in the ladle, but a higher percentage of uranium in the steel requires addition in the furnace, or chilling will occur. These results were obtained in the electric furnace, but uranium can also be made in the crucible furnace. Uranium steel has not come into general use, although some of the steel makers claim that uranium is a satisfactory substitute for tungsten in certain cases.

Analytical Methods for Uranium.—There are a number of methods suitable for the analysis of uranium ores, and these are discussed at length in *Bulletin* 70 of the U. S. Bureau of Mines. One of the best methods which is particularly applicable to ores such as carnotite is as follows: Treat from 2 to 5 g. of ore, according to the proportion of vanadium, iron, and uranium present, in a covered beaker, with 10 c.c. of HCl and let it stand 15 min., shaking it occasionally. Add 5 c.c. of HNO_3 and heat on a steam bath. When the solution is quiet, remove the cover and evaporate to dryness. Add 3 c.c. of HCl and 5 c.c. of water to the residue and let it stand on the steam bath for a few minutes, stirring occasionally. Dilute with 25 c.c. of hot water, filter into a small beaker, and wash the residue with warm water. Some ores do not yield all the vanadium to this treatment, a little remaining with the insoluble residue.

To make sure that all vanadium is in solution, ignite the residue in a platinum dish, treat it with 5 c.c. of HF, and evaporate to dryness on a steam bath. Do not bake the residue, for it is not necessary to expel all SiO_2. Add 3 c.c. of HCl to the residue from the HF treatment and evaporate to dryness. Repeat this treatment to insure expulsion of HF. Treat the residue with 2 c.c. of HCl and 2 c.c. of water and stir with a glass rod until any red crust is dissolved, then dilute the solution with water and filter it into the main liquid. Pass H_2S into the liquid to separate copper, lead, and other metals of this group, filter and boil the liquid to expel the H_2S. Concentrate the liquid to 100 c.c. if necessary, oxidize it with an excess of H_2O_2, and then neutralize with dry Na_2CO_3, adding 2 or 3 g. in excess. Boil the liquid for about 15 min. until the yellowish uranium precipitate dissolves, leaving a brown precipitate which is principally iron. Filter and wash the iron precipitate with water, reserving the filtrate. Dissolve the iron precipitate in the least possible amount of HNO_3 (1:1), and add 10 c.c. of H_2O_2, neutralize with Na_2CO_3, add an excess of 2 g. of Na_2CO_3, and boil as before. Filter into the beaker containing the first filtrate.

[1] HABER and LE ROSSIGNOL, *Zeit. Elektrochem.*, 1913, Vol. **19**, p. 53.
[2] *Bull.* A. I. M. E., August, 1918, p. 1366.

The iron precipitate may contain a little vanadium—reserve it for further treatment. Evaporate the united filtrates from the iron precipitation to a volume of about 200 c.c., add 10 c.c. of strong HNO_3 and boil until all CO_2 is expelled. Neutralize the free acid with ammonia (until a slight permanent precipitate appears), then add 4 c.c. of HNO_3 for each 100 c.c. of liquid. Now add 10 c.c. of a 20 per cent lead acetate solution, and enough of a strong solution of ammonium acetate to neutralize the nitric acid present and substitute acetic acid for it. The object is to precipitate the vanadium as lead vanadate in an acetic-acid solution. The ammonium-acetate solution may be made by mixing 80 c.c. of strong ammonia, 100 c.c. of water, and 70 c.c. of acetic acid 99 per cent pure. Heat the liquid containing the lead vanadate, precipitate on the steam bath for 1 hr. or more, filter on a tight filter, and wash with warm water. Dissolve the precipitate in the least possible quantity of hot dilute nitric acid, neutralize as before, add 3 c.c. of nitric acid in excess, add 2 c.c. of lead-acetate solution and repeat the precipitation of lead vanadate by adding ammonium acetate in excess, filter and add the filtrate to the one from the first precipitation of lead vanadate.

Reserve the precipitate of lead vanadate for treatment as described below. Evaporate the united filtrates from the lead vanadate to about 400 c.c. Add 10 c.c. of strong H_2SO_4 to separate the bulk of the lead (derived from the excess of lead acetate) as $PbSO_4$, filter and wash the precipitate with cold water. Neutralize the filtrate from the $PbSO_4$ with ammonia and add freshly prepared $(NH_4)HS$ until the solution is yellow and the uranium and what little lead is present are precipitated as sulphides. Warm the mixture on a steam bath until the sulphides settle well. Filter and wash slightly with warm water. Dissolve the precipitate in a No. 2 beaker with hot dilute (1:2) HNO_3, add 5 c.c. of H_2SO_4 and evaporate till fumes of H_2SO_4 appear, cool and take up with water, boil, and let the small precipitate of $PbSO_4$ settle until the solution is cold, filter the precipitate and wash it with very dilute H_2SO_4. Nearly neutralize the filtrate with ammonia, have the solutions cool (not warmer than 30°C.), and add powdered carbonate of ammonia in about 2 g. excess to precipitate the aluminum. Let the precipitate settle over night, filter, and wash it with warm water. If the precipitate is bulky or is at all yellow, dissolve it in a little dilute H_2SO_4 and reprecipitate with carbonate of ammonia as described. Acidulate the filtrate from the alumina with H_2SO_4, and boil thoroughly to expel CO_2. Active boiling for ½ hr. is required. Make the liquid slightly alkaline with NH_4OH while it is hot, and heat on the water bath until the ammonium uranate collects and settles. Filter and wash with a very dilute (2 per cent) solution of $(NH_4)NO_3$. Do not allow the precipitate to run dry on the filter after the first washing. Dry the precipitate, ignite it in a porcelain crucible, and weigh as U_3O_8. Dissolve the precipitate in HNO_3 and test it with H_2O_2 for vanadium and with $(NH_4)_2CO_3$ for aluminum. Dissolve the lead vanadate in dilute HNO_3, add 10 c.c. of H_2SO_4, and evaporate the mixture to fumes. Cool, take up with water, add 10 c.c. of a concentrated solution of SO_2 to the mixture, boil until the excess of SO_2 is expelled, and titrate the hot solution with a standard solution of potassium permanganate. The vanadium compound is reduced by SO_2 from V_2O_5 to V_2O_4. The iron equivalent of the permanganate solution multiplied by 1.6264 = the V_2O_5 equivalent.

It is not necessary to filter out the lead sulphate before boiling the mixture to expel the SO_2. The boiling is best done in a large flask. The iron precipitate that was produced by the addition of Na_2CO_3 and H_2O_2 to the original acid solution may contain vanadium. Ignite the precipitate in a platinum crucible and fuse the residue with Na_2CO_3. Leach the fused mass with water, filter, and acidulate the filtrate with H_2SO_4. The filtrate may be added to the main solution before reducing with SO_2, or reduced and titrated separately, as preferred. In expelling the excess of SO_2, it is

necessary to boil the liquid for at least 10 minutes after the smell of SO_2 can no longer be detected, or until the fumes do not decolorize dilute $KMnO_4$ solution. Some of the factors used in calculations are: Fe value of permanganate times 0 9133 = V. Fe value of permanganate times 1.6294 = V_2O_5. 1.78431V = V_2O_5. U = 0.84808 U_3O_8

TUNGSTEN

(Atomic weight = 184)

Occurrence.—There are four reasonably common tungsten minerals found in the United States. Ferberite, wolframite and hübnerite are closely associated as regards their composition. Ferberite is usually classed as an iron tungstate, although it may and often does carry moderate quantities of manganese. Wolframite is an iron-manganese tungstate carrying usually, however, more iron than manganese. Hübnerite is a manganese-iron tungstate containing more manganese than wolframite. These minerals form a complete series with almost an infinite number of members between a pure iron tungstate and a pure manganese tungstate.

Hess[1] has suggested the following definitions: "Ferberite should be considered as an iron tungstate ($FeWO_4$) contaminated by not more than 20 per cent $MnWO_4$, a proportion equivalent to 4.69 per cent MnO, or 3.63 per cent Mn in the pure tungsten mineral. Hübnerite should be considered as managnese tungstate ($MnWO_4$) contaminated by not more than 20 per cent $FeWO_4$, a proportion equivalent to 4.74 per cent FeO, or 3.69 per cent Fe. Wolframite should cover the ground between the limits above indicated. That is, wolframite should be considered a mixture of iron and manganese tungstates containing not less than 20 per cent nor more than 80 per cent of either. Except the light-colored hübnerites, most of these minerals can not be detected by the eye or by simple tests, and in the absence of analyses it is, therefore, convenient to refer to the dark minerals of the series as wolframites." Ferberite and wolframite when pure are black. When partly oxidized they may appear brownish from the presence of iron oxide. Hübnerite is characteristically brown, some specimens however, being yellowish, others reddish and some nearly black. These minerals are all monoclinic in form. Ferberite has more of a tendency to form well defined crystals than do the others. In hardness, all of these minerals are a little over 5. Their specific gravities range from 7 2 or 7.3 in hubnerite to 7.5 in ferberite, while the specific gravity of wolframite is intermediate between these figures. Scheelite is a calcium tungstate ($CaWO_4$). In color it is usually white, light-gray, or light-yellow, although its color may occasionally vary from greenish-yellow to brown. Its luster is slightly glassy. It is found in granular masses, or irregular lumps of a more or less coarse texture. Its hardness is a little less than 5, and its specific gravity is approximately 6. It possesses four directions of good cleavage. Other tungsten minerals of less importance are stolzite or lead tungstate, cuprotungstite or hydrated copper tungstate, and tungstite or tungstic ocher, a hydrated tungstic oxide.

Ferberite is found in several western states, but mainly in Colorado in the Boulder district. This district has a length of 12 miles in a northeast and southwest direction, and a width of about 7 miles, and begins about 6 miles due west of the town of Boulder. The tungsten veins are in many ways similar to the gold veins of the district, and seem to have a close connection with them in genesis. Hübernite and wolframite are mainly found in New Mexico, Arizona, Nevada and South Dakota, although the

[1] U. S. Geol. Surv. *Bull.*, No. 652, p. 22.

minerals are frequently met with in small quantities in other states. They do not form as important a commercial source of tungsten as ferberite and scheelite. The latter mineral is mainly found in California, principally near Atolia in northwest San Bernardino County. A second area of considerable importance lies in Inyo County, near Bishop. The Atolia-Randsburg district occupies an area of about 2½ by 10 miles in extent. Tungsten minerals are found to a very considerable extent in foreign countries, namely, in Burma, Siam, the Malay States, Portugal, Boliva, Argentina, Peru, England, China, Australia and New Zealand. During the last few years, ores from these countries have competed to a very considerable extent with United States ores.

Extraction from the Ores.—Up to recent years, most methods of treatment of tungsten ores were small modifications of the original Oxland process which was patented in 1847. This involves a fusion with sodium carbonate of the finely ground ore previously leached with hydrochloric acid to get rid of traces of bismuth if this metal is present. Sometimes a small amount of sodium nitrate is added to the sodium carbonate. The mixture is placed in a reverberatory furnace and sintered, care being taken not to fuse it. It is then removed and ground. Frequently, this treatment does not give a sufficiently high extraction of the tungsten, and involves a second sintering process. The sintered mass is leached with hot water in tanks. Tungsten dissolves as sodium tungstate, while the iron, calcium and most of the manganese remain insoluble. Some of the phosphoric acid and silicic acid also dissolve as silico- and phospho-tungstates. Traces of manganese may also dissolve, owing to the sodium nitrate present, as sodium manganate. The solution of sodium tungstate may be either evaporated to dryness, or evaporated to the point at which crystallization takes place. The chief impurities are sulphates, silicates and arsenates of sodium, with traces of iron and manganese. Iron, manganese and arsenic are precipitated by a small quantity of caustic soda, and the greater portion of the sodium sulphate will crystallize out before sodium tungstate. The silica remains in the mother liquor, after the crystallization of the sodium tungstate, and causes some loss of tungsten in the form of soluble silico-tungstates, which, however, can be used as by-products for fireproofing purposes. The fairly pure sodium tungstate is redissolved in boiling water and added to a boiling solution of hydrochloric acid made up of 1 part of concentrated acid and 7 of water. Sometimes about 5 per cent of nitric acid is added. The result is the precipitation of the tungsten as hydrated tungstic oxide, which is filtered off and washed in filter presses. It is important that the oxide should be washed free from sodium salts, as otherwise on drying it has a greenish tinge which is not attractive to purchasers.

One of the best methods, if not the best, for producing a high-grade tungstic acid is that of Ekeley and Stoddard (U. S. Pat. No. 1,255,144). This process is used at one mill in Boulder County for the treatment of medium grade ferberite ores and concentrates. Usually middlings from the mills, or ore running from 15 to 25 per cent WO_3 are used. The product is a high-grade tungstic acid said to contain less than 0.03 per cent phosphorus and 0.03 per cent sulphur, with only a small per cent of silica. After drying the oxide runs from 99 to 99.7 WO_3. The ore is mixed with sodium carbonate and salt and the charge is placed in sheet-iron pans 2 by 4 ft. and 6 in. in depth. This is placed in a firebrick furnace heated by oil burners. The charge is so proportioned that a glass slag is obtained. The heat treatment requires about an hour, at the end of which the pans are pulled out of the furnace onto an iron

rack, clamped and inverted, and the fused charge dumped into an iron receptacle where it is allowed to cool. It is broken into pieces and ground in a crusher to approximately ½-in. size. It is then mixed in a cement mixer with a hot-water wash liquor from a previous run. The contents are dumped into a screen-bottom trough which retains the coarse residue. This is shoveled back into the mixer and washed with hot water; the wash water being used in the next run. The concentrated solution is allowed to settle and the clear solution is given a secret treatment which removes the last traces of the phosphorus, arsenic, silica and other deleterious substances. This probably involves the use of magnesium chloride as a precipitant. After filtering, the clear solutions are run into a large wooden tank, heated and calcium tungstate is precipitated by the addition of a solution of calcium chloride. The precipitate is allowed to settle, scraped out and treated with commercial hydrochloric acid in a wooden revolving drum. After settling, the solution is drawn off through suction filters. The residue is treated twice with hydrochloric acid in this manner and finally the whole is dumped onto the suction filters. This treatment produces tungstic acid as a precipitate, and the acid solution contains calcium chloride and calcium sulphate. This is allowed to run into stone vessels where the calcium sulphate crystallizes out, and the clear solution is drawn off into barrels where lime is added, which produces calcium chloride for further use.

Acid-leaching methods are also used in connection with all the commercial tungsten ores. They are especially applicable to getting rid of manganese and give good results with scheelite. Ferberite, wolframite and hübnerite are soluble in hot concentrated hydrochloric acid, but it is necessary to digest the ores in the acid for a considerable time. Under such conditions the ores are decomposed and the manganese goes into solution while the tungsten is precipitated as tungstic acid and remains with the insoluble residue. After filtering, the residue is extracted with ammonia which dissolves the tungstic acid, giving ammonium tungstate. On ignition this is decomposed giving tungstic acid and ammonia which may be recovered for further use. Phosphorus is gotten rid of at some stage in the operation by precipitating with magnesium chloride, or if tungsten powder is made from the tungstic acid, a considerable amount of phosphorus can be leached out of the powder with hydrochloric acid. Scheelite is soluble in hydrochloric acid, but one firm adds to the ease of solubility by using hydrochloric acid and sodium chlorate. The decomposition of the ore takes place in acidproof earthenware pots in a hood with a steam draft. After complete decomposition the tungstic acid and insoluble silica are filtered off. By using high-grade scheelite the amount of silica present is not large, and the refining of the product is not carried any further, but the acid without further removal of the silica is used for the manufacture of tungsten powder.

Gin[1] suggests a bisulphate fusion for the ore whenever tin is present. This method, therefore, does not apply specially to American ores, but is useful for some of the foreign ores. The tin can be largely separated from the tungsten ore by means of magnetic separation, but there is usually at least 1 per cent of tin oxide left behind with the tungsten. The ore is decomposed by means of acid potassium sulphate in a muffle furnace. After the sulphate is fused, the ore is thrown in and the mass is stirred continually and the temperature increased until the whole mass is fluid enough to run out of the furnace. After solidification the fused mass is ground and treated with water, which dissolves the soluble sulphates and phosphoric acid and leaves insoluble potassium acid tungstate as a white amorphous precipitate. About 50 per cent excess of bisulphate over that theoretically required is actually necessary. The insoluble residue is dried and treated with a warm solution of ammonium carbonate, or cold ammonia water in which carbon dioxide is passed. The potassium

[1] *Trans. Am. Electrochem. Soc.*, Vol. 13, p. 481.

acid tungstate dissolves leaving the silica, the cassiterite and the insoluble sulphates. The solution is evaporated to crystallization, which gives ammonium tungstate from which tungstic oxide is made by heating.

Concentration Methods.—The tungsten minerals are all very amenable to concentration methods, the methods used involving jigs, tables and slimers. A good many mills also have "rag plants," instead of slimers, or work the two together. The average grade of concentrate that was demanded up to 2 or 3 years ago was around 60 per cent. Recently (1918) concentrates of 55 per cent were classed as high-grade. One of the difficulties in connection with milling operations is the handling of second-jig and low-grade slime products. These to a certain extent have been taken care of by a chemical treatment plant. Where this is not used, the product, of course, is often reground and reconcentrated, but this always involves considerable loss. Mill operations have been improved very much during the last 5 years, and an average recovery of 85 to 87 per cent is not now uncommon.

Tungsten Compounds.—Tungsten forms two definite oxides, namely, tungsten dioxide (WO_2) and tungsten trioxide (WO_3). These combine together to form more complex oxides. The dioxide is formed when a current of hydrogen is passed over the trioxide at dull-red heat. Under these conditions, different colored oxides are obtained, including the dioxide. It may also be prepared in the wet way by reducing the trioxide by means of zinc and hydrochloric acid. The dioxide is a brown powder of specific gravity of 12.1. It is strongly pyrophoric and must be cooled in hydrogen before exposure to air. It is slightly soluble in hydrochloric acid and sulphuric acid, giving purple solutions. It is soluble in sodium and potassium hydroxides giving the alkaline tungstates with the evolution of hydrogen. Tungsten trioxide is prepared by heating ferberite or scheelite with concentrated hydrochloric acid for a considerable time, as already described under "extraction from the ores." It can also be prepared by adding hydrochloric or nitric acids to a solution of sodium or potassium tungstate, the hydrated oxide (tungstic acid) being precipitated. On ignition this gives the trioxide. It is a bright canary-yellow colored amorphous powder which becomes dark-orange on heating, but regains its color on cooling. A small amount of sodium salt gives a greenish tint to the oxide, which is difficult to remove. It slowly becomes greenish on exposure to light. It can be obtained in the crystalline state by igniting a mixture of sodium tungstate and carbonate in a current of hydrogen chloride when the trioxide is obtained in olive-green prisms. The specific gravity of the oxide is 6.34. The trioxide is an acid-forming oxide and yields two tungstic acids, namely, the normal acid (H_2WO_4) and metatungstic acid ($H_2W_4O_{13}$). In addition to the salts corresponding to these acids, a large number of other tungstates have also been prepared, of which the following are a few:

$$M_2WO_4 = M_2O.WO_3$$
$$M_2W_2O_7 = M_2O.2WO_3$$
$$M_2W_3O_{10} = M_2O.3WO_3$$
$$M_2W_4O_{13} = M_2O.4WO_3$$
$$M_2W_5O_{16} = M_2O.5WO_3$$
$$M_2W_6O_{19} = M_2O.6WO_3$$

Tungstic acid (H_2WO_4) is formed as a white precipitate when a soluble tungstate is treated with an acid in the cold. If, however, an excess of hot acid be used, H_2WO_4 separates as a yellow powder, insoluble in water and all acids except hydrofluoric. Metatungstic acid ($H_2W_4O_{13}.7H_2O$) is prepared by decomposing the barium salt with dilute sulphuric acid. It crystallizes in small yellow octohedra which lose their water of crystallization at 100°C, and on ignition are converted into the trioxide. The crystals are soluble in water. Normal sodium tungstate ($Na_2WO_4.2H_2O$) is prepared by fusing the tungsten minerals with soda ash and treating with water. It crystallizes as thin rhombic prisms, soluble in four parts of cold and in two parts of boiling water. Heated to 200°C., sodium tungstate becomes opaque and loses its water. It fuses at a red heat. Sodium metatungstate ($Na_2W_4O_{13}.10H_2O$) is formed by boiling the normal salt with tungstic acid for a considerable period. It crystallizes in octahedra belonging to the regular system. It is soluble in about 10 times its weight of cold water.

Metallic Tungsten.—Metallic tungsten can be made in a number of ways. The purest product is obtained by heating a very high-grade tungstic oxide in a current of hydrogen. The oxide can also be reduced by means of carbon or metallic zinc. Metallic aluminum and magnesium also can be used instead of zinc. Most metallic tungsten prepared commercially is in the form of powder for making tungsten steel. Reduction with carbon is the method usually used as the reaction goes readily and presents few difficulties. The reduction can take place either in a steel tube or in a covered steel crucible. Davis[1] has carefully studied the conditions and temperatures necessary for the reduction of tungstic oxide to the metal. He finds that at 650 to 850° the oxide goes to a black or purple on heating with carbon; at 950 to 1050°C. a chocolate-colored product is the result (probably WO_2); and at temperatures above 1050°C. the gray powdered metallic tungsten results. The ratio of tungstic oxide to carbon varies from 10:1 to 10:1.6 depending upon the process used, the temperature of reduction and the time involved. A small excess of carbon can be partially removed by washing. Both fireclay crucibles and iron tubes give satisfactory results, and a product of over 98 per cent metallic tungsten can be produced. Whereas the reduction to metal is complete at 1050°C., it is better to keep the temperature around 1,100°C.

Davis also found that the temperature of reduction with hydrogen at ordinary pressures is much the same as with carbon. The properties of metallic tungsten are so unique that when it was first prepared it led to a search for methods for producing the metal in a ductile form. It was found that this could be done by repeated heating, rolling, hammering, drawing and swaging. Cast tungsten, or tungsten powder, differs widely in its properties from the pure raw material, such as is used in the manufacture of incandescent lamp filaments. The tungsten powder is brittle, crystalline and hard and has a specific gravity of 16 to 17. The pure metal is softer and tougher, can be welded at a yellow heat, and even drawn into fine wire. Its specific gravity is 18.8, and the melting-point close to 3,270°C. A wire of 5 mm. in diameter has a tensile strength of more than 450,000 lb. to the square inch. At a red heat, the metal oxidizes in the air. Melted sulphur and phosphorus attack it slowly; potassium bisulphate, caustic alkalis and fused nitrates attack the metal, but solutions of these salts have practically no action on it. Hot dilute sulphuric acid affects it only slightly, but the concentrated acid dissolves the metal slowly. At ordinary temperatures

[1] *Jour. Ind. Eng. Chem.*, Vol. 11, No. 3, p. 201.

hydrochloric acid of any concentration has practically no action; but the strong boiling acid dissolves it slowly. Concentrated nitric acid and hydrofluoric acid have very little action on tungsten, but the two acids when mixed attack it fairly rapidly.

Ferrotungsten.—Tungsten is the principal rare metal used for alloy purposes in connection with the manufacture of high-speed steels. In making this steel, either ferrotungsten or tungsten powder may be used. The annual production of the two is probably about equal in quantity. When ferberite is used, practically all ferrotungsten is made directly from the high-grade concentrate without previous chemical treatment of the ore. The product obtained in such a case contains usually from 70 to 85 per cent tungsten, 0.5 per cent carbon, 0.4 per cent silicon, 0.5 per cent manganese, 0.01 per cent sulphur, and 0.02 per cent phosphorus. Ferrotungsten has a high density, fine gray fracture and is not crystalline.

Keeney[1] gives a detailed description of the manufacture of ferrotungsten. The reduction with carbon goes readily. The slag may contain as high as 8 per cent FeO, but less than 1 per cent WO_3. Theoretically, the reduction of 100 parts of alloy from 122 parts of ferberite requires 16 parts of carbon, but practically about 25 per cent excess of carbon is charged. Small amounts of lime and fluorspar are used to flux the silica. Operating in this manner, with an excess of carbon, a product is made containing 3 per cent carbon, 70 per cent tungsten, 0.05 per cent phosphorus and 0.01 per cent sulphur, with slag containing below 1 per cent WO_3. The analysis of a typical concentrate for the manufacture of such a product is WO_3, 60.36 per cent; Fe, 22.0; SiO_2, 8.0; Mn, 0.05; S, 0.35 and P, 0.05 per cent.

A typical operation involves charging into the furnace 65 lb. of a mixture composed of 200 lb. concentrate, 42 lb coke, 56 lb. lime and 6 lb. fluorspar. Three more 65-lb. charges are added at intervals of ½ hr., and at 2½ hr. from the start the furnace is tilted and the slag poured. This cycle is repeated until a 1,200-lb. button has been formed, requiring 24 to 36 hr. The furnace is allowed to cool, is torn down and the button of metal removed, cleaned and broken up. This crude metal is refined as follows: A charge of 150 lb. metal and 75 lb. ferberite concentrate are smelted for ½ hr., when 12 lb. of fluorspar are added. After another 3 hr. the slag is poured and a fresh charge is started. The process is continued for from 36 to 48 hr. until a button weighing 1,500 lb. has been formed, when the furnace is allowed to cool, is torn down and the button of metal removed, cleaned and broken. Ferrotungsten containing less than 1 per cent carbon can be made in a single smelting operation by careful regulation of the carbon in the charge and the use of an acid slag. The product, however, is less pure and the slag loss is higher. In addition, the metal will contain higher phosphorus and sulphur.

Uses of Tungsten.—The main use for tungsten is in the manufacture of steel, especially high-speed steel. Such steel is generally made by the crucible process, although not always. A steel suitable for such use may contain as high as 15 or 20 per cent tungsten, and as low as 8 or 10 per cent tungsten, and 4 per cent chromium. Vanadium and molybdenum may also be used in small quantity, and uranium has in some special steels partially replaced the tungsten. Tungsten is also used in self-hardening steels, or those requiring no tempering after forging. They may have a composition between the following limits: Tungsten, 2.4 to 3.4 per cent; chromium up to 6 per cent; carbon 0.4 to 2.2 per cent and silicon 0.2 to 3 per cent.

The chief property which tungsten gives to steels is tensile strength, which, with the elastic limit, increases within certain limits as the percentage of tungsten increases.

[1] *Bull.* A. I. M. E., August, 1918, p. 1338.

Elongation and resistance to shock diminish proportionately, and the hardness increases fairly consistently with the per cent of tungsten. Tungsten is also used for filaments in electric lamps. For making the filaments the "squirting" process was originally employed. This involved mixing metallic tungsten powder with an organic binding material, such as gum, and these were squirted into the filament. The carbon was eliminated by placing the filament in an atmosphere containing a volatile compound of tungsten, such as the oxychloride, and a small quantity of hydrogen. On heating the filament by an electric current, the carbon was replaced by tungsten.

Another method consists in mixing metallic tungsten powder with an amalgam containing equal amounts of cadmium and mercury and squirting the mixture through a die in the usual way. The cadmium and mercury in the filament are volatilized by heating and the filament retains the usual brittleness, but after continued heating at higher temperatures the filament becomes pliable and can be bent. Drawn filaments are now used; the drawing being made possible by hammering, heating, swaging, etc. Tungsten is also a constituent in the so-called "bronze powders" employed for decorative purposes, and has also been used to a small extent in the fireproofing of cloth and other fabrics, as a mordant for silk, and for coloring glass and porcelain.

Analytical Methods for Tungsten.—Tungsten in ores can be determined quantitatively by the following method: The ore ground as finely as possible in an agate mortar is fused with from 5 to 10 times its weight of sodium-potassium carbonates and extracted with hot water. If any gritty particles remain, another fusion is necessary. An equal volume of concentrated hydrochloric acid is added to the aqueous solution of the alkaline tungstate, and the whole evaporated to dryness, after which the silica is dehydrated by heating at 120°C. for an hour. The residue is moistened with hydrochloric acid, taken up with water and boiled; then filtered and washed with 5 per cent HCl or ammonium-nitrate solution. The filtrate contains a small amount of tungsten, which is determined by heating the filtrate and the washings to boiling and adding 5 to 6 c.c. of a cinchonine solution made by dissolving 25 g. of cinchonine in 200 c.c. of 1:1 HCl. This is allowed to digest on a hot plate while the other operations are being performed.

The precipitated tungstic oxide is dissolved in hot ammonia solution (Watt's solution of 200 c.c. strong ammonia, 1,000 c.c. water, 10 c.c. HCl), filtered into a platinum dish, the filtrate being washed with the ammonia solution and evaporated to dryness and ignited. The cinchonine precipitate is filtered and washed with hot dilute cinchonine solution (100 c.c. water to 5 to 6 c.c. of the above solution), dried and ignited in the platinum dish with the tungstic oxide. A few drops of sulphuric acid and a little HF are added, and the SiO_2 driven off at a dull red heat. The tungsten is weighed as WO_3. Small quantities of impurities may be removed by treating the WO_3 with the ammonia solution, filtering and again igniting.

Ferrotungsten can be analyzed by the following method which is used at the laboratories of the Tungsten Products Company at Boulder, Colo.

The refined ferrotungsten, crushed and rolled to pass a ½-in. mesh screen, goes to a machine which automatically mixes, samples and sacks the product for shipment. The sampler is of type developed by this company, which cuts one-fifth of the total mix. This cut passes through the machine again after being rolled to approximately ¼-in. mesh. If the original mix is very large the operation is repeated to bring the weight of the sample down to less than 500 lb. This final sample from the automatic is passed repeatedly through a riffle sampler until the last cut weighs 15 to 50 lb. This goes to the laboratory sampling department where it is reduced in a steel mortar to pass a 3/16-in. screen. The pounding necessary for this process is done by a 2-in.

Ingersoll Rand piston drill set up vertically in a frame above the mortar and pestle in such a manner that it is used as an air hammer. The sample is thoroughly mixed and split twice, and one-quarter is then further reduced to pass a 10-mesh screen. This procedure of screening, mixing and splitting is continued through a series of screens until the last portion passes the 200-mesh screen giving the analyst about 100 g. of finely powdered metal. The operation of reducing a 20-lb. sample received from the smelter to a 100-g. laboratory pulp of 200-mesh powder by this system requires about 1 hr.

For the determination of tungsten, two 1-g. samples are mixed separately in nickel crucibles with about 5 g. sodium peroxide and a cover of sodium carbonate. Fusion is done in an electric muffle at about 800°C. which requires 6 to 7 min. to make a perfect decomposition. Cool, leach out in water in covered 400 c.c. beakers. Remove crucibles and acidify carefully with hydrochloric acid using a moderate excess. Add about 2 c.c. nitric acid or H_2O_2 to assist in dissolving any small fragments of nickel oxide scale and bring to a boil. Most of the tungsten separates as H_2WO_4 and all iron and nickel salts are in solution. Add about 40 c.c. cinchonine solution, stir and let stand in a warm place for about 4 hr. or preferably over night. This precipitates all the remaining tungsten as cinchonine tungstate, and it has proved to be just as effective a reagent for this purpose as quinine hydrochloride. Filter off the settled precipitate through a 15 cm. close weave paper arranged over a platinum cone and suction flask. Wash thoroughly with warm dilute cinchonine wash water using gentle suction. No trouble will be experienced due to the precipitate sticking to the beaker if a few drops of hydrofluoric acid are used.

The washed precipitate is transferred to a shallow gold dish of known weight and ignited to WO_3 in the muffle. Cool, moisten with 10 or 12 drops of hydrofluoric acid to remove any traces of SiO_2 which might be carried down, dry and ignite again. Weigh and calculate to W. The factor is 0.793. Duplicate determinations carried out in this way should check to within 0.10 per cent. The proportions used in the cinchonine solution are 50 g. of cinchonine alkaloid dissolved in 2 liters of cold water containing 150 c.c. hydrochloric acid; for the cinchonine wash water, 100 c.c. of above cinchonine solution and 50 c.c. hydrochloric acid diluted to 1 l. with hot water and used from a bulb wash bottle is convenient. For the determination of carbon—ferrotungsten and tungsten metal powder burn completely and readily in oxygen—and carbon is easily determined in any type of combustion train. In the laboratory mentioned they prefer to catch the CO_2 in a Meyer bulb in 2 per cent barium-hydrate solution, to filter, wash and weigh the $BaCO_3$.

The usual fusion-oxidation methods of determining sulphur are all open to objections when applied to a ferro alloy or other material whose sulphur content is below 0.05 per cent. The blank is always high, due to traces of sulphates in fluxes and reagents used and the danger of picking up fumes or traces of sulphuric acid from the apparatus of a general laboratory. The sulphur content of ferrotungsten occurs as sulphides which, in a finely ground sample, are completely decomposed yielding H_2S. This suggests at once the application of the method which has been used successfully for 2 years. Two to five grams of 200-mesh ferrotungsten or metal powder are weighed into an evolution flask. Cover with 50 c.c. water and add 25 c.c. strong hydrochloric acid by way of the separatory funnel. Heat to boiling and boil for about 10 min. catching the evolved gas, air and steam in ammoniacal cadmium-chloride solution. The usual yellow precipitate of cadmium sulphide shows the presence of sulphides in the alloy. Wash the cadmium-chloride solution from the bulbs, then cool, acidify with hydrochloric acid and titrate at once against a weak iodine solution (1 c.c. = 0.0005 g. sulphur) using starch as an indicator. The iodine solution is standardized by using a Government standard steel of known sulphur content, or by using a ferrotungsten of known sulphur content. Boiling with dilute hydrochloric acid does not

dissolve the alloy, but does decompose the sulphides present as may be shown by filtering off the contents of the evolution flask after the operation and examining for sulphur by a fusion method or by a combustion method.

The removal of phosphorus from the alkaline liquor after a fusion decomposition of ferrotungsten presents certain difficulties. Precipitation with magnesia mixture from dilute solutions is incomplete unless much time is allowed for this step, also precipitation from concentrated solutions either as magnesium-ammonium phosphate or as aluminum phosphate tends to drag down some tungsten, involving another step for its removal. To avoid these difficulties the use of uranium acetate has been introduced at this stage. The precipitation is quantitative from moderately dilute solutions and no dragging down of tungsten occurs. Weigh 1 g. sample into a nickel crucible containing 6 to 8 g. chemically pure Na_2O_2. Mix thoroughly and cover with about 1 g. of chemically pure Na_2CO_3. Ignite in a muffle to complete fusion of the fluxes. Cool and leach out carefully with warm water in 250 c.c. covered beaker. Remove crucible and partly neutralize the NaOH with 25 c.c. HCl (1–3) to permit filtering without dilution. Stir and then allow the dense $Fe(OH)_3$ to settle out while standing on a warm plate. Decant off through a 12½-cm. qualitative paper into a 600-c.c. beaker. Wash precipitate into the filter, allow it to drain thoroughly then give it two good washes with hot water stirring up the precipitate well with a fine jet. Reserve this precipitate of $Fe(OH)_3$ which contains a small amount of phosphorus, to add to the uranium precipitate obtained from the tungsten solution.

Acidify the filtrate of sodium tungstate and sodium phosphate with acetic acid using 30 c.c. of 40 per cent acetic. Add 2 c.c. of 5 per cent uranium-acetate solution. Boil off all CO_2. Make just alkaline with NH_4OH (1:1). This will require about 20 c.c. The precipitate is ammonium-uranyl phosphate. Add 2 c.c. more uranium acetate which precipitates at once as uranium hydroxide and serves to drag down the last traces of phosphate, as well as to assist in filtering the ammonium-uranyl phosphate. Boil off any large excess of NH_4OH. Filter through a qualitative paper and wash twice with hot water to remove tungsten. Place the precipitate in the same beaker together with the iron precipitate obtained above, add 30 c.c. water and 25 c.c. strong nitric acid. Boil until both precipitates are in solution and the filters reduced to pulp. Filter into a 500-c.c. Erlenmeyer flask washing the pulp once with hot water. Add 5 c.c. of 5 per cent $KMnO_4$ solution to acid filtrate. Boil to oxidize all phosphorus to H_3PO_4. Clear of MnO_2 by adding 2 c.c. H_2O_2 (1:1). Boil to remove excess H_2O_2 and cool under the tap. Add 45 c.c. NH_4OH (1:1) which will nearly neutralize the nitric acid, then 50 c.c. of molybdate solution. Stopper the flask and shake for 5 min., and let stand at least 15 min. before filtering. Filter through a 9-cm. filter. Wash with acid ammonium-sulphate wash solution to remove all nitro-molybdate. Dissolve the yellow phospho-molybdate in hot dilute ammonia water which must be free from chlorides, into the same Erlenmeyer flask. Wash the paper well with alternate washes of ammonia water and hot water. When cool, acidify with 5 c.c. of H_2SO_4 (1:1) and pass through the reductor, following with a thorough wash of cold water. Titrate against standard $KMnO_4$ solution to the same end point as used in determining the reductor blank. The iron value of the standard permanganate solution times 0.0163 equals the P value. The ammonium-sulphate wash solution must be distinctly acid. A good formula is: H_2SO_4 (1:1) 100 c.c.; NH_4OH (1:1) 60 c.c.; water, 2 l. If convenient it is well to allow the precipitate of yellow phospho-molybdate to stand about 1 hr. after shaking for 2 min. A blank on all reagents including a fusion of Na_2O_2 and Na_2CO_3 should be carried through with the determinations. It is sometimes desirable to add a measured quantity of dilute phosphate solution of known P content to the blank for close work. Checks should agree within 0.015 per cent P.

MOLYBDENUM

(Atomic Weight = 96)

Occurrence.—The chief commercial minerals of molybdenum are: Molybdenite (MoS_2); wulfenite ($PbMoO_4$) and molybdite ($Fe_2O_3.3MoO_3.7½H_2O$). Of lesser importance are ilsemannite, possibly ($MoO_3.SO_3.5H_2O$), belonesite ($MgMoO_4$), and powellite ($CaMoO_4$). The first three are the only ones from which molybdenum is obtained commercially. Molybdenite contains 59.5 per cent molybdenum and 40.05 per cent sulphur. It is a soft, opaque, lead-gray mineral with metallic luster. It frequently occurs in flakes or scales resembling some micas as regards its cleavage. In hardness it ranges from 1 to 1.5, and readily leaves a mark on paper of a bluish-gray color. Its specific gravity is from 4.7 to 4.8. The mineral is widely distributed throughout the United States, especially in the West, and whereas it is found in a large number of localities in small quantities, there are also several large deposits which are being worked commercially.

The most important of these is at Climax, Colorado, near Leadville. Here a large portion of a mountain is impregnated with the mineral, and whereas the grade averages less than 1 per cent MoS_2, the amount of ore available is very large. Another large deposit is on Red Mountain, near Empire, Colo., about 50 miles due west of Denver. There are two mills at Climax and one at Red Mountain. Smaller deposits of molybdenite are found in several places in the United States, especially in Arizona, New Mexico, Nevada, California, etc. Wulfenite contains theoretically 26.15 per cent of molybdenum and 56.42 per cent of lead. It is a brittle, heavy, semi-transparent mineral with resinous lustre and is generally of a wax or orange-yellow color, although occasionally it is olive-green, yellowish-gray or even brown. Its hardness is 2.75 to 3, and its specific gravity is 6.7 to 7. It crystallizes in a tetragonal system, and the crystals are commonly square and tabular, and are sometimes very thin. Less frequently, they are octahedral or prismatic. Like molybdenite, wulfenite is widely distributed in the western states; probably the largest known deposit is at the Mammoth mine, Mammoth, Arizona, from which a very considerable tonnage of concentrates has already been obtained. It is, however, found in numerous other places in Arizona, Nevada and to some extent New and Old Mexico. Molybdite is a hydrous ferric molybdate, lemon-yellow to pale-yellow in color, and occurs as an earthy powder, usually as incrustations. Molybdite is an alteration product of molybdenite, probably formed by the interaction of molybdic acid and limonite; the molybdic acid being an oxidation product of the molybdenite.

Molybdite, therefore, is frequently found associated with molybdenite, especially where the latter mineral has had a chance to weather. Molybdenum minerals are found in notable quantities in several foreign countries. Molybdenite is found in Queensland, New South Wales, Norway and Canada. It has only been during the last 3 years (written 1919) that the United States has produced concentrates of molybdenum minerals in commercial quantities. Up to that time practically all of the world's production came from Queensland, New South Wales and Norway.

Extraction from the Ores.—As ferromolybdenum, which is the chief use for molybdenum, can be made directly from molybdenite concentrates, it is not necessary to treat molybdenite chemically unless molybdic oxide or ammonium molybdate are required for chemical purposes. In such a case, the molybdenite may be roasted to oxide, treated with ammonia which dissolves the molybdic

oxide as ammonium molybdate, filtered and evaporated to dryness, or to crystallization of the ammonium molybdate. On ignition the ammonia is driven off and may be recovered for further use. Doerner (U. S. Pat. 1,299,560) gives an oxidizing roast to a mixture of molybdenite and salt. The presence of the sulphur in the charge, together with the oxidizing atmosphere which is maintained during the treatment, results in the liberation of free chlorine in two stages. In the first stage, the sulphur in the charge is converted by the oxidizing roast into sulphur dioxide, and in the second stage, the sulphur dioxide together with additional oxygen reacts with the chloride to liberate chlorine. This reacts with the molybdenum, forming volatile compounds, either the chlorides, oxychlorides or mixtures. The chlorides and oxychlorides pass off to a condensing chamber and are decomposed into molybdic oxide and hydrochloric acid by the action of steam or water.

Wulfenite is a more difficult metallurgical problem than molybdenite. This mineral nearly always carries small quantities of vanadinite, and the two can not be separated mechanically. Kissock first used a sodium carbonate fusion method in a small blast furnace. The wulfenite mixed with sodium carbonate and coke was strongly heated and the lead was obtained as metallic lead, while the molybdenum went into the slag in the form of sodium molybdate. This slag was used directly in the electric furnace for the making of ferromolybdenum, but the excess of sodium carbonate had very decided and deleterious effects on the furnace linings. Holladay (U. S. Pat. 1,281,961) prepares a sodium molybdate slag reasonably free from lead and other impurities, then leaches the slag with water, and adds dilute calcium-chloride solution in the cold. This precipitates most of the impurities which are still present, while the molybdenum stays in solution. On filtering and boiling and adding excess calcium chloride, the molybdenum is precipitated as calcium molybdate which can be used for the preparation of molybdic oxide, or can be used directly in the making of molybdenum steel. Conditions for the precipitation of calcium molybdate have been studied carefully by Bonardi.[1]

Concentration Methods.—Molybdenite can be concentrated readily by flotation methods. An ore carrying less than 1 per cent can be concentrated to a product carrying 60 or even 70 per cent molybdenite. Usually mixtures of kerosene and pine oil are used although other oils give satisfactory results on certain ores. Wulfenite can be concentrated by ordinary milling methods, using tables and slimers. The mineral crushes readily, but an ore carrying as little as 0.5 per cent MoO_3 as wulfenite can be concentrated with a fair recovery. Vanadinite which is frequently associated with it can not be separated to form very satisfactory products as the specific gravities of the two minerals are almost the same.

Molybdenum Compounds.—The molybdenum oxides are the sesquioxide (Mo_2O_3), molybdenum dioxide (MoO_2) and molybdenum trioxide (MoO_3). The first two oxides are basic and little is known concerning them except their halogen derivatives. The trioxide is the important oxide and is not only used commercially but also gives rise to the molybdates. It is a white powder which on heating becomes yellow. It melts at a red heat to a dark-yellow liquid and this on cooling solidifies to a yellowish-white crystalline mass with a specific gravity of 4.39. It volatilizes at high temperatures when heated in closed vessels, but sublimes readily in the air, giving small transparent rhombic tables. It is

[1] *Chem. and Met. Eng.*, Sept. 15, 1919.

soluble in 500 parts of cold water and 960 parts of hot water; the solution being slightly acid to litmus.

Molybdic acid ($H_2MoO_4.H_2O$) may crystallize out when a solution of ammonium molybdate is treated with nitric acid. The addition of a crystal of the compound renders the separation more easy. Normal sodium molybdate (Na_2MoO_4) is formed by fusing the trioxide with sodium carbonate. It crystallizes from water in acute rhombohedra containing 2 molecules of water. Below 6° it contains 10 molecules of water of crystallization. The dimolybdate ($Na_2Mo_2O_7$) is formed when sodium carbonate and the trioxide are fused in the correct proportions. The tetramolybdate ($Na_2Mo_4O_{13}.11H_2O$), the octomolybdate ($Na_2Mo_8O_{25}.4H_2O$) and the decamolybdate ($Na_2Mo_{10}O_{31}.12H_2O$) are of lesser importance. Normal ammonium molybdate, $(NH_4)_2MoO_4$, is produced when molybdenum trioxide is heated with excess of concentrated ammonia. It crystallizes in four-sided prisms which are decomposed by water. If a solution of the trioxide in ammonia is evaporated the compound $(NH_4)_6Mo_7O_{24}.4H_2O$ crystallizes out in monoclinic crystals. This is the salt which is usually known as "ammonium molybdate."

Metallic Molybdenum.—Metallic molybdenum may be prepared by reducing molybdic oxide with aluminum powder or by heating the trioxide or one of the chlorides in a current of hydrogen. It may also be prepared by heating a mixture of molybdenum trioxide with $\frac{1}{10}$ of its weight of sugar charcoal in an electric furnace in a carbon crucible. The pure metal is malleable and is not hard enough to scratch glass. It has a specific gravity of about 9 and can be forged when hot. It oxidizes readily at a dull red heat and is attacked by fused potassium chlorate, nitrate, etc.

Ferromolybdenum.—The raw materials for ferromolybdenum may be either molybdenite, molybdic oxide, a sodium-molybdate slag, or calcium molybdate. The reducing agent is usually carbon although 90 per cent silicon material ground to 60 mesh has been used. Lime and fluorspar are used as fluxes. The reaction that takes place with molybdenite is as follows:

$$2MoS_2 + 2CaO + 3C = 2Mo + 2CaS + 2CO + CS_2.$$

Reduction with silicon metal gives the following reaction:

$$MoS_2 + Si = Mo + SiS_2.$$

According to Keeney[1] for about 100 parts of molybdenite, 58 parts of lime are necessary for slagging the sulphur as calcium sulphide. The reaction works closely to the theoretical, and there is no difficulty in making a product with about 0.1 per cent sulphur and from 1½ to 3 per cent carbon. With sodium-molybdate slag, the reaction is as follows:

$$Na_2MoO_4 + 3C = Mo + 3CO + Na_2O.$$

The reduction of sodium molybdate requires considerably more power than the reduction of the sulphide or oxide. The average power consumption is 7 to 7½ kw.-hr. per pound of molybdenum produced. The recovery varies from 78 to 80 per cent with a loss of 10 per cent in the slag and 10 per cent mechanically by volatilization. Ferromolybdenum containing 80 per cent molybdenum and under 1 per cent carbon can not be regularly tapped from the electric furnace.

[1] *Bull.* A. I. M. E., August, 1918, p. 1334.

Uses of Molybdenum.—The main use of molybdenum is in making molybdenum steel. Undoubtedly, the introduction of molybdenum into steel increases the elastic limit without diminishing its ductility. Molybdenum also may replace tungsten in high-speed steels. Up to recently, only from 0.5 to 2 per cent molybdenum was used, but recently the amount has been considerably increased. High-speed molybdenum steel can be welded with difficulty and is quite brittle on forging. Magnetic steel contains from 2½ to 3 per cent molybdenum and about 1 per cent carbon. A chromium-molybdenum steel has been used recently quite extensively in connection with certain automobile parts, especially where resistance to heavy wear is required, such as in bearings, etc. Such a steel contains 0.2 to 0.6 per cent Mo. Ammonium molybdate is used extensively in chemical laboratories. Some salts of molybdenum are also used for coloring glazes in porcelain and to some extent in coloring silks, leather and rubber.

Analytical Methods for Molybdenum.—The following method has been worked out by Messrs. Bonardi and Barrett of the U. S. Bureau of Mines: Weigh 0.25 to 5.0 g. of the finely pulverized ore into a 250 c.c. Erlenmeyer flask. Add 15 c.c. of HNO_3 and heat until the brown fumes are gone. This will be found to be the most rapid manner of decomposing the sulphides present. Carefully add 5 to 10 c.c. of HCl and heat about 20 min, or until the ore is completely decomposed. Wash down the sides of the flask with hot water and heat about 5 min. longer. Cool. Add 5 to 10 c.c. excess NH_4OH, heat a few minutes and filter hot, washing with hot water. If the residue of insoluble, iron and aluminum hydroxides is large, it is advisable to puncture filter and wash residue into flask in which decomposition was made, add sufficient HCl to dissolve the precipitated hydroxides, make slightly ammoniacal, heat and filter into the same beakers used for the first filtration. Wash well with hot water. This second treatment is made in order to prevent an appreciable amount of molybdenum being held mechanically in the residue. In case the ore should carry lead, as wulfenite for example, decompose with HNO_3 and HCl as previously stated, but after cooling add 10 c.c. of H_2SO_4 and evaporate to dense fumes. Cool, add about 50 to 60 c.c. of water and heat to dissolve soluble sulphates. Cool. Filter to remove insoluble lead. Wash well and add to the filtrate 5 to 10 c.c. excess NH_4OH, heat and filter. Repeat this precipitation in order to insure extracting all the molybdenum from the residue.

If considerable phosphorus is present, it should be removed by adding a few cubic centimeters of magnesia mixture to the ammoniacal solution before filtering off the iron and aluminum hydroxides. The ammoniacal solution should be warmed about 20 min. to allow the precipitated magnesium phosphate to settle. If not removed, the phosphorus will precipitate as lead phosphate along with the lead molybdate. The molybdenum is now in the form of ammonium molybdate in a solution practically free from silica, iron and alumina, also lead in case the sample was taken to fumes with H_2SO_4. The solution should have a volume of about 250 c.c. Make acid with HCl using methyl orange as an indicator, adding about 5 c.c. excess. Add 5 to 10 g. of sodium or ammonium acetate. This amount will be sufficient to destroy any free mineral acid. It has been found that the use of HCl to neutralize the NH_4OH and the addition of 5 c.c. excess followed by sodium or ammonium acetate in sufficient quantity to destroy the mineral acid produces the proper conditions for the precipita-

tion of the molybdenum as $PbMoO_4$ so that the precipitate will be granular, will settle rapidly, and will be easily filtered and washed. The addition of a very small amount, about 8 drops, of HNO_3 before precipitating the molybdenum as $PbMoO_4$ has been advocated by Weiser.[1]

Precipitation is best made by titrating this hot solution with a lead acetate solution (about 18 g. crystallized lead acetate per liter) until a test drop gives no color change with a drop of tannic-acid solution. Add about 2 c.c. excess lead acetate, 2 or 3 c.c. of acetic acid, and place the beaker back on the hot plate for about 15 to 20 min. to allow the precipitated $PbMoO_4$ to crystallize and settle. Filter hot and wash well with hot water. It has been suggested by Weiser that the precipitate be washed twice by decantation with a 2 per cent solution of NH_4NO_3 and then be transferred to the filter paper and washed with $(NH_4)NO_3$. By following the above details a precipitate of $PbMoO_4$ will be obtained which will settle rapidly and is easily filtered and washed. It will also be a very pure $PbMoO_4$. The washed filter is placed in a fireclay annealing cup and ignited at a dull-red heat in a muffle. The filter need not be previously dried. After cooling, the precipitates are brushed out of the annealing cups onto the balance pan and weighed. Weight of $PbMoO_4$ times .2615 gives weight of molybdenum.

THORIUM

(Atomic Weight = 232.4)

Occurrence.—The principal commercial mineral carrying thorium is monazite, although small quantities of thorianite and thorite have been used commercially. These latter minerals, however, are limited in quantity. Monazite is composed mainly of phosphates of the cerium and lanthanum earths together with a variable percentage of thoria. Its specific gravity is from 4.8 to 5.5, and its color varies from yellow-gold to reddish-brown and is occasionally even dark-brown or black. Monazite occurs in certain gneissic and granitic rocks, but the actual commercial deposits which are worked are alluvial. The principal sources are Brazil and India, although the mineral has been mined successfully in the United States, in the Carolinas, Idaho and Florida. It has been found in Switzerland, Africa and in Australia, and to a limited extent in river rocks and placers in Ekaterinburg, Russia.

Monazite is usually found in gravels of small streams and in bottom lands. In Brazil and India, it occurs mainly in the beach sands of sea water. It is found in small crystals in gneiss, granite and pegmatite rocks. As these rocks become disintegrated the crystals are washed into the creeks and streams and together with other heavy sands are deposited in the beds of water courses. On the coast of Brazil the monazite from the crystalline rocks of the coast mountains is concentrated in the sea sands by the waves of the sea. The bulk of the monazite in Brazil is found in the states of Espirito Santo and Bahia. In India, the main location is in the Travancore district in Southern India. The deposits of the Carolinas in the United States cover an area of several hundred square miles east of the Blue Ridge Mountains. Practically all of the monazite mined in the Carolinas is derived from the gravel in the streams and bottom lands, the miners usually following the course of the streams and creeks. The gravels vary greatly in thickness; in general they are between 1½ and 2½ ft. thick. Monazite is also found in Florida.

[1] *Jour. Phys. Chem.*, Vol. 20, 1916, p. 640.

Extraction from the Ores.—The methods of treating monazite for the production of thorium nitrate are more or less secret and are changed from time to time, depending upon conditions, costs of chemicals, etc. The general principles of the commoner method used before the war are as follows: The mineral is heated in cast-iron pans or pots with about twice its weight of concentrated sulphuric acid, until the monazite is completely decomposed, giving a white mass of sulphates which are largely insoluble in the acid. This mixture is run into cold water in a lead-lined vat and the whole stirred until solution is complete. The material is allowed to stand for a considerable period in order that the insoluble matter consisting of silica, zircon, rutile and other minerals insoluble in concentrated sulphuric acid, may settle out, and the solution which contains the rare earths, phosphates, etc., is decanted off. If now the free acid is partially neutralized so as to reduce the acidity, thorium phosphate is precipitated first owing to the fact that it is less soluble than the phosphates of the other rare earths. The thorium phosphate still carrying quantities of other rare-earth phosphates is filtered, dissolved in a minimum amount of acid, and the fractional precipitation repeated.

One method of still further purifying the precipitate is to boil it with oxalic acid which causes the thorium to be precipitated as thorium oxalate, while the phosphoric acid remains in solution. The precipitated phosphates are digested for a prolonged period with sodium hydroxide and the hydroxides formed are dissolved in hydrochloric acid. If the acid solution is then carefully treated with sodium hydroxide, until about one-sixth of the bases have been precipitated, thorium hydroxide will be precipitated before the other hydroxides. Baskerville has suggested the volatilization of the phosphoric acid by mixing 1 part of monazite with 1.1 parts of petroleum coke, 0.8 parts of lime and 0.15 parts of fluorspar, and heating in an electric furnace. This not only removes the phosphorus but also gives the latter in a marketable form. Further purification of the thorium hydroxide may be carried on in one of several ways. The oxalate method depends upon the fact that thorium oxalate forms a double salt with ammonium oxalate which is soluble, while cerium oxalate is almost insoluble. The carbonate method is based upon the fact that thorium carbonate forms double salts with the alkali carbonates which are soluble, whereas the double salts of the cerium earth oxalates are insoluble. The sulphate method depends upon the fact that certain hydrated sulphates of thorium possess a considerable difference in solubility from the sulphates of the cerium earths. This fact is used as a basis for fractional crystallization. Whichever method is used, after the thorium is sufficiently purified it is converted into thorium carbonate or hydroxide and dissolved in nitric acid and the solution evaporated until thorium nitrate, $Th(NO_3)_4.4H_2O$, crystallizes out. After the beginning of the war, owing to the greatly increased cost of certain chemicals, especially oxalic acid, considerable modifications were necessary in the process used for treating monazite sand. These changes in practice have been kept secret, but consist essentially in combinations of the methods described above.

Concentration Methods.—The first stage of concentration in the Carolinas involves the use of oscillating tables or sluice boxes. The concentrates produced in the sluice boxes contain 20 to 60 per cent monazite. The crude concentrates must be further refined, and are best treated by electromagnetic separators, of which the Wetherill type has proved to be the most successful.[1] The separation of the minerals is dependent upon the difference in their magnetic permeability.

[1] GUNTHER: "Electromagnetic Ore Separation," 1909.

The magnets are best adjusted so that the first pole of the first magnet removes from the sand the highly magnetic material, as for instance, the magnetite and ilsemannite; the second pole of the first magnet extracts the garnets and also the finer grains of the ilsemannite; the third magnet (being the first pole of the second magnet) removes all of the coarser grains of the monazite; and the last pole extracts the finer grains of the monazite. At the end-turn of the rubber belt of the machine, the residues are dropped into a receptable.[1] The grade of the concentrates obtained from the different large sources of supply varies considerably. The average concentrate obtained in the Carolinas was about 3½ to 4 per cent thorium oxide, whereas that obtained from Brazil averages around 6 per cent. It was for this reason very largely that the industry in the Carolinas was ultimately given up. The monazite from India has even a higher grade than that from Brazil, averaging around 9 per cent thorium oxide, and some of it going still higher. As concentrate of this type carries about 27 per cent cerium oxide, 29 per cent lanthanum and allied oxides, and 2 to 4 per cent yttria and allied oxides. It also contains about 26 per cent phosphoric acid.

Thorium Compounds.—Thorium hydroxide, $Th(OH)_4.xH_2O$, is precipitated from solutions of thorium salts by means of ammonia or alkalis. It is a white gelatinous precipitate, soluble in excess of the reagent. A granular product is obtained if crystallization is carried out below 30°C. Thorium dioxide, ThO_2, can be made by ignition of the hydroxide, the nitrate, etc. The oxide is insoluble in dilute acids. Thorium sulphate, $Th(SO_4)_2$, can be obtained by evaporating to dryness a solution of the dioxide in sulphuric acid. The sulphate forms double salts with the sulphates of the alkali metals; it crystallizes in transparent monoclinic crystals with nine molecules of water of crystallization above 43°C. Below this temperature it has four molecules. Thorium nitrate, $Th(NO_3)_4.12H_2O$, crystallizes at ordinary temperatures in large tablets, soluble in water and alcohol. It also may be obtained with six and five molecules of water of crystallization by crystallization from a hot-water solution and from a nitric acid solution. The nitrate is the most important commercial salt of thorium. It forms double nitrates of the general type $R'_2Th(NO_3)_6$ where R′ = NH_4, K, Rb, Cs, and $R''Th(NO_3)_6.8H_2O$, where R″ = Mg, Mn, Zn, Ni, Co.

The thorium phosphates which are obtained by the addition of phosphoric acid or alkali phosphates to solutions of thorium salts are of somewhat doubtful composition. Thorium oxalate, $Th(C_2O_4)_2.6H_2O$, may be precipitated quantitatively by the addition of oxalic acid to a thorium salt even in the presence of considerable quantities of mineral acids. It is much less soluble in mineral acids than the oxalates of the rare earths. The salt dissolves in excess of alkali oxalate, but it is precipitated from the solutions by mineral acids.

Metallic Thorium.—The metal has probably not yet been prepared in a perfectly pure state. Reduction of the oxide with magnesium is never complete, and attempts to reduce with carbon give a mixture of the metal and carbide. Moissan and Honigschmid heated the purified anhydrous chloride with sodium in a sealed glass tube and obtained a product which was said to contain only 3 per cent of the oxide. The amorphous metal is a dark-gray powder of specific gravity 11.3 and when hammered and strongly heated, it has a density of 12.16.

[1] K. L. KITHIL: *Technical Paper*, 110, U. S. Bureau of Mines.

It burns readily in air, and melts at about 1,700°C. although the pure metal would probably melt at a higher temperature.

Uses of Thorium.—The main use of thorium is in connection with the incandescent gas-mantle industry. The successful use of incandescent gas mantles began in 1893 when Welsbach patented the use of a mixture containing 98 to 99 per cent thorium oxide with 1 to 2 per cent cerium oxide (English Pat. 124 of 1893). With this mixture the oxides give a brilliant light and have a maximum illuminating power. The cerium oxide is probably in solid solution in the thorium oxide.[1] Thorium oxide is a very poor heat conductor and hence can be raised to a high temperature. The small amount of cerium oxide gives enough color for efficient light emission. An outline of the methods used for obtaining mantles is as follows: The mantle itself is made either of ramie fiber or of artificial silk. The woven mantles are thoroughly washed in a 2 per cent solution of nitric acid, distilled water, and then in dilute ammonia. The latter is thoroughly washed out by distilled water. The mantle is dried in a current of hot air and then dipped in a solution of thorium and cerium nitrates, consisting of 99 per cent thorium salt and 1 per cent of cerium.

Small quantities of beryllium or magnesium nitrate are added for strengthening purposes. The upright mantles are then fitted with an asbestos loop by which they are suspended, whereas the inverted mantles are fixed to a supporting ring. Those portions on which there is especial strain are sometimes treated with a thorium solution containing much larger proportions of calcium, aluminum, or magnesium salts. The mantle is then shaped and burnt off from the top downward by applying a Bunsen flame. During this process of burning off, there is considerable shrinkage. As soon as the carbonization is finished, the mantle is shaped and heated with low-pressure burners, after which it is hardened by heating in a high-pressure burner. The mantles now consisting of nothing but the ash skeleton are immersed in a collodion solution containing collodion, ether, camphor and castor-oil. The ingredients may vary to some extent. After drying at a moderate temperature, they are ready for use.

[1] WHITE and TRAVERS: *Jour. Soc. Chem. Ind.*, 1902, Vol. **21**, 1012.

SECTION XXVIII

RARE GASES

By Richard B. Moore[1]

HISTORY

Discovery of Argon.—It is a curious fact that during the 30 or 40 years immediately preceding the discovery of argon, little work was done by chemists on the atmosphere. They seemed to feel that here at least an end had been reached, and the wise man should bend his energies in other directions. No suspicion was entertained that the air was a veritable gold mine for chemical research, and even after the evidence seemed to indicate that we had not yet found out all there was to know about our atmosphere, there was a feeling of doubt and uncertainty that made the work move slowly. The first clue to the undiscovered elements was partly accidental. In 1882 and several succeeding years, Lord Rayleigh worked on the relative densities of hydrogen and oxygen. In 1893 he published his results on the densities of some other gases, notably those of oxygen, nitrogen and air.[2] He prepared oxygen and nitrogen by different methods; and while the density of oxygen proved in all cases to be the same, that of nitrogen prepared by chemical methods differed from that of nitrogen obtained from the air. The latter was about 0.5 per cent heavier than the former. A difference of this magnitude could not be accounted for on the basis of experimental error, and the riddle remained unanswered for some time. Finally, Prof. (afterwards Sir) William Ramsay asked permission of Lord Rayleigh to take up the matter from the chemical standpoint. He had already in some previous work found that red-hot magnesium was a good absorbent for nitrogen. He concluded that if there was any part of atmospheric nitrogen different from the rest, a separation might be made by passing the gas over the heated metal. This was tried, the oxygen first being removed by metallic copper. A slight increase in the density of the product was observed. Arrangements were now made to circulate the gas backwards and forwards over the heated magnesium. After several days of this treatment the density was found to be 16.1. At this stage Ramsay did not know that he had to deal with a new element, but thought that the results were due to a triatomic form of nitrogen, corresponding to ozone. A further absorption by magnesium finally gave a gas with density of about 20. It was only when the spectrum of this product was examined that Ramsay became convinced that he had found a new element. Meanwhile, Lord Rayleigh was dealing with the problem in a different manner. He passed sparks through a mixture of atmospheric nitrogen and oxygen in the presence of a solution of sodium hydroxide. The hydroxide absorbed the oxides of nitrogen formed, and after removal of the excess of oxygen, the resulting gas showed an increased density. From this point, Ramsay and Rayleigh continued the work together and announced the discovery of the new element "argon" at the British Association Meeting in 1894.

[1] Chief chemist, Bureau of Mines, Washington, D. C.

[2] *Proc. Roy. Soc.*, 1893, Vol. **53**, p. 146; 1894, Vol. **55**, p. 340.

Discovery of Helium.—After the discovery of argon, Ramsay looked for other sources of the element. He heard through Sir Henry Miers of a paper by W. F. Hillebrand of the U. S. Geological Survey, in which it was stated that the mineral cleveite, on heating, gave off a considerable quantity of inactive gas which was supposed to be nitrogen. Ramsay suspected that this gas might be argon and so obtained a sample of the mineral; heated it with sulphuric acid; pumped off the evolved gas; sparked it with oxygen, and finally ran it into a spectrum tube. The spectrum was entirely different from that of argon; having as a chief characteristic a bright-yellow line. At first Ramsay's surprise was so great that he thought there was something wrong with the spectroscope. In addition, others suggested various explanations for the bright-yellow line; the most common being that it was the sodium line due to dirty electrodes, or other causes. It was only when the spectrum of the sodium flame was compared through a comparison prism with the yellow line from the spectrum tube that it became evident beyond question that a new element—namely, terrestrial helium—had been discovered.

Discovery of Krypton.—It now seemed probable that other undiscovered gases beside argon and helium existed. After a large number of minerals had been examined, in addition to the gases from mineral waters, as well as sea water, which were investigated with the object of finding all possible sources of argon, helium and any new gases, Ramsay, assisted by his pupil Travers, decided on the fractionation of a considerable quantity of argon. Fifteen liters of the latter gas had previously been prepared in connection with the work on helium, and it was planned to use this for the investigation. Before it was fractionated, however, a liter of liquid air, presented by Dr. Hampson, was allowed to evaporate and the last fraction of gas was collected separately. The spectrum of this gas, after purification from nitrogen and oxygen, showed a bright-green and a bright-yellow line not belonging to the argon spectrum. The density of the sample was also greater than that of argon, and the new element was called krypton.

Discovery of Neon.—It was natural with this encouragement that the work should be carried on with great eagerness. With the assistance of Dr. Travers, the 15 l. of argon referred to above was now fractionated. The first fraction which came off, containing the gases with the lowest boiling points, was separated and examined. The spectrum showed a large number of brilliant red and yellow lines, and the density of this particular sample was about 15. The new gas was called neon. Apparatus was now devised in connection with the Hampson liquid-air machine, with which the lighter fractions from liquid air could be reliquefied and refractionated. Finally, a portion was obtained which could not be liquefied even by air boiling under reduced pressure. This proved to consist largely of neon, but also contained helium—proving the existence of the latter gas in the air. All attempts to separate the helium from the neon were futile, until later on the two were fractionated at the temperature of liquid hydrogen. At this temperature the neon solidified and the helium could be pumped off.

Discovery of Xenon.—The residues or last fractions from 30 l. of liquid air which had been allowed to evaporate, were afterwards used to make a larger quantity of krypton. The majority of the gas consisted of argon which was carried through a rigorous course of fractionation; the last fraction containing the kryptons showing some new blue lines, with a density greater than that of krypton. After careful refractionation, the final gas obtained gave a density of 64, and the

new element was called xenon. The density put this gas in its proper place in the periodic table. The volume of xenon obtained was only 3 c.c., while the total volume of krypton recovered was 12 c.c. All of the physical constants of these gases were afterwards found with the small volumes indicated; and only men possessed of the manipulative skill of Ramsay and Travers could have done this.

General Properties of the Gases.—The main property common to all the rare or "noble" gases is the fact that they are absolutely inert to chemical action. So far, no attempts at getting them to combine with other elements have been successful. When Ramsay first obtained argon in quantity, he used rigorous methods to act on it chemically. He sparked it with oxygen, chlorine and hydrogen without success. Red-hot sodium hydroxide, sodium peroxide, or fused potassium nitrate had no action. Fluorine, nascent chlorine, and red-hot magnesium were equally ineffective. Helium, neon and the other gases appeared to be just as inactive as argon. More recent attempts to get argon to combine with other elements involved an arc discharge between electrodes of different metals immersed in pure liquid argon. Whereas the metals usually underwent a decided change themselves, in no case could it be proved that any argon compounds had even a momentary existence. And yet there is some evidence that possibly compounds may be formed under certain conditions. Fergusonite is a mineral which, on heating, evolves considerable quantities of helium.[1] In doing so, it becomes quite hot; and Ramsay called it an "endothermic mineral." Again, when a discharge is passed between the electrodes of ordinary spectrum tubes containing the rare gases, there is a very decided tendency for the electrodes to "splash" (*i.e.*, from a mirror coating) on the sides of the tubes. This coating adsorbs the gas and shortens the life of the tube. This "splashing" would seem to indicate that endothermic compounds were momentarily formed. The ratio of the specific heats indicates that every one of the rare gases is monatomic. Additional evidence to this effect is furnished by the results of Sir J. J. Thomson's "Rays of Positive Electricity."[2]

Position in the Periodic Table.—The inert gases constitute a group by themselves. Their atomic weights do not fit anywhere in the periodic table, unless a place can be found in the eighth group, or by themselves in a new group preceding group one. The latter position has been preferred and accepted by all chemists. Usually the chemical properties of an element have a direct connection with its position in the periodic table. The fact that the rare gases are inert chemically fully justifies placing them is a separate group by themselves. Argon is the only one of the rare gases which appears to be out of place with the arrangement of the table as given above; its atomic weight being higher than that of potassium, the element which follows it. It is not, however, out of place as regards its atomic number. Originally it was thought that argon was probably a mixture, and vigorous efforts were made to separate it into two or more compounds. One plausible explanation has been advanced—that argon contains a small percentage of diatomic molecules; 5 per cent of such molecules would reduce its density to 19 and the atomic weight to 38. Such a condition is not inconceivable, but if it were a fact the density of the gas would probably vary with the tempera-

[1] When the zirconium silicate from the Buckman & Pritchard property near Jacksonville, Fla. is ground, it suddenly evolves helium after reaching a certain fineness.—EDITOR.

[2] SIR J. J. THOMSON: "Rays of Positive Electricity," Longmans, Green and Company, 1913.

ture, which is not true. The ratio of the specific heats for argon is 1.659, which closely approximates the theoretical 1.667 for a perfect gas. Five per cent of diatomic molecules should give a ratio of 1.648, instead of 1.659. No satisfactory explanation, therefore, can be advanced at the present time for the anomalous position of argon in the periodic table.

HELIUM

Homogeneity of the Gas.—The discovery of helium by Ramsay has already been described. Before long some doubt was cast upon the elementary nature of the gas and on its identity with solar helium. When the gas was allowed to stream through a porous plug into a Plücker tube, the light at first was green, the line λ 5,016 of the single-line group being equal in intensity to the D_3 line, and then gradually became yellow as D_3 became relatively stronger.[1] Runge and Paschen, who made the observation, concluded that they had separated the gas obtained by Ramsay from cleveite into two components: Helium of density 2.2, and a lighter gas for which a name "parhelium" was proposed. Some claims were also made that helium obtained from different minerals showed considerable variations in density[2] and that by diffusion the gas could be separated into fractions differing still more in density. The homogeneity of helium was satisfactorily proved by Travers,[3] who showed that on passing an electrical discharge through helium in a vacuum tube, the pressure fell steadily, owing to the fact that the gas was adsorbed by the finely divided platinum which was deposited on the walls of the tube; and that with this fall in pressure, the color of the glow changed from orange-yellow to bright-yellow, then to yellowish-green, and finally to green. The tube was then allowed to cool; the remaining gas was pumped out, and the tube was then heated in order to drive out the gas which had been occluded by the platinum. This gas showed exactly the same behavior as the original gas when a discharge was again passed through the tube. Ramsay and Travers also carried out some elaborate experiments in fractionating by diffusion the gas obtained from cleveite. They showed conclusively that whereas fractions of different densities could be obtained, this variation was due to the presence of argon; and the elementary nature of helium was, therefore, firmly established.

Occurrence.—Kayser[4] was the first one to detect the presence of helium in the atmosphere by spectroscopic methods, and his results were confirmed by Friedlander,[5] Ramsay's original determination of the quantity in the atmosphere was one volume of helium in 250,000 volumes of air.[6] Watson,[7] with better facilities at his command, calculated that the amount is more probably 1 part by volume of helium in 185,000 volumes of air. Helium is occluded in a large number of minerals; indeed it is contained to a greater or lesser extent in all minerals and rocks. As will be explained more fully later, Ramsay and Soddy[8] showed that the radium emanation gave rise to helium. The question

[1] RUNGE and PASCHEN, *Phil. Mag.*, 1895, Vol **40**, p. 297.
[2] RAMSAY, *Proc. Roy. Soc.*, 1896, Vol **59**, p. 325.
[3] *Proc. Roy. Soc.*, 1897, Vol. **60**, p. 449.
[4] *Chem. News*, 1895, Vol. **72**, p. 89.
[5] *Zeit. physik. Chem.*, 1896, Vol. **19**, p. 657.
[6] *Proc. Roy. Soc.*, 1905, Vol. A, **76**, p. 111; 1908, Vol. A, **80**, p. 599.
[7] *Trans. Chem. Soc.*, 1910, Vol. **97**, p. 810.
[8] *Proc. Roy. Soc.*, Vol. **72**, p. 204; Vol. **73**, p. 346.

received still further light when Rutherford and Geiger proved the identity of the alpha particle given off by radioactive changes with the helium atom. The helium found in the earth's crust, therefore, is undoubtedly partly, if not entirely, due to the disintegration of radioactive types of matter in the earth's crust with the elimination of alpha particles. Generally speaking, the amount of helium in minerals is proportionate to the amount of uranium or thorium present. The Hon. R. J. Strutt has, therefore, sought to determine by this means the age of certain minerals and rock deposits with fair success. In some cases, however, the rate of leakage is greater than the rate of formation from radioactive changes.

Helium is found in the gases evolved from many mineral springs, notably the Bath springs in England, the springs at Mazières, at Monte Irone (Albano), at Raillière in the Pyrennes, at Wildbad in the Black Forest, and in a number of springs in Tuscany. In some cases the gases evolved carry as much as several per cent of helium. The most notable source of helium in quantity, however, is certain natural gases in the United States. Cady and MacFarland[1] showed that a number of natural gases in Kansas contained as much as 1 per cent or even more of helium. At Dexter in Cowley County, Kansas, the content of some wells was as high as 1.8 per cent. At Eureka, samples were analyzed containing as high as 1.5 per cent, and in the El Dorado field certain of the wells contained as much as 1¼ per cent helium. The Augusta field was almost as rich as the others. In certain localities in Oklahoma natural gas samples carry as much as ½ per cent helium, while in Vinton County, Ohio, about 80 miles south of Columbus, there is a very large supply of gas containing between 0.4 and 0.5 per cent helium. The most satisfactory supply at present in this country, however, is at Petrolia, Tex., 20 miles northeast of Wichita Falls. The gas here carries 0.93 per cent helium, and as much as 15,000,000 or 20,000,000 cu. ft. a day of natural gas can be pumped. There are several small sources of supply in Europe. One test well near Pechelbronn, in Alsace, carried 0.4 per cent helium. The gas in Transylvania has less than 0.002 per cent, but it is claimed that the gases from some of the fumaroles in Italy are reasonably rich in helium.

All radioactive minerals carry helium to a greater or less extent. The amount of helium in the mineral depends on the amount of uranium or thorium, the age of the mineral itself, and also on the physical properties of the mineral, which affect its power of occlusion of helium. Since the radioactive minerals are those which carry uranium or thorium, all minerals containing these elements also contain helium, provided the gas is not able to diffuse out so fast as it is formed.

Liberation of Helium from Minerals.—Helium can be obtained from minerals either by strongly heating, or by solution in acids. A still better method is to fuse the mineral with acid sodium sulphate. Whichever method is used, the tube containing the mineral is connected with a Töpler pump, and the evolved helium may be taken through the pump and collected over mercury. A high temperature is required to get rid of all of the gas by heating alone. In case of monazite, it has been shown that very little gas comes off at 500°C., and at 900°C. it took 24 hr. of heating to liberate all the gas. For thorianite, 0.7 per cent came off at 350°C. after 5 hr. heating, 8.5 per cent at 500°C. after 80 hr., and the whole at 1,000° after 30 hr.

Purification.—Helium can best be purified by means of charcoal at liquid air temperature. If the gas containing traces of nitrogen, oxygen, carbon

[1] *Jour. Am. Chem. Soc.*, 1907, Vol. **29**, p. 1523.

dioxide, or other similar impurity, is run into an evacuated tube containing cocoanut charcoal, the tube having previously been heated and pumped dry by means of an efficient air-pump, all other gases but the helium will be adsorbed and the helium can be pumped out in practically a pure condition. If argon is present, it will also be adsorbed by the charcoal, but in the case of neon, only partial adsorption will take place and some neon will probably come over with the helium unless the quantity is very small. In order to get a complete separation it is, therefore, necessary, actually to fractionate the two, using the above method.

Properties.—Helium is a colorless gas, is odorless and tasteless.[1] Its *density* is 1.995, according to Watson.[2] The *compressibility coefficient* at zero is −0.0006 between pressures of 400 and 800 mm. of mercury.[3] The *molecular weight* and therefore, the *atomic weight* calculated from Heuse's value for the density is 4.0. Helium does not obey Graham's law of diffusion of gases, but passes through a porous diaphragm more slowly than is expressed by the law. The *solubility* of helium in water was determined by Antropoff,[4] who found for the *absorption coefficient* the value 0.0134 at zero, and 0.0226 at 50°, with minimum at 10°. The *thermal conductivity* of helium is 0.00003386.[5] The *refractivity* was first determined by Rayleigh and afterwards more accurately by Ramsay and Travers, who found it was 0.1238 times that of air, which gave the value for helium of 1.000361.[6] The *viscosity* was first determined by Rayleigh by measurement of the rate of flow of the gas through a capillary tube. He found the value 0.96; air being 1.0. Schultz redetermined the *viscosity* and found it to be 1.086 times that of air at 15°C.[7] The *spectrum* of helium has been studied by Runge and Paschen, by Watson and others. The lines fall naturally into groups, in each of which we have a principal series, and two subordinate series. One of these groups consists of doublet series and the line (D_3) is the first in the principal series. It is the lines of this group which characterize the solar spectrum of helium, and are seen when an ordinary vacuum tube containing helium is examined with a spectroscope. Generally speaking, all of the lines are seen in a vacuum tube, but the relative intensity of the lines varies with the pressure and, therefore, the color of the tube itself may vary materially with different pressures. The main helium line, usually called the "helium yellow," consists of a double line with the wave lengths 5876.21 and 5875.88.

Formation of Helium from Radioactive Substances.—The fact that helium is formed from radium was proven by Ramsey and Soddy.[8] By dissolving a soluble radium salt in water, it was found after purification of the evolved gas that an appreciable residue of helium was left behind. By allowing the solution containing the radium salt to stand, the helium was reformed and could be pumped off again. The origin of helium in the air has always been ascribed

[1] Ramsay and Travers, *Proc. Roy. Soc.*, 1898, Vol. **62**, p 316.

[2] *Trans. Chem. Soc.*, 1910, Vol. **97**, p. 810. It is 1 999, according to Heuse (*Ber. deutsch. physikal. Ges.*, 1913, Vol. **15**, p. 518).

[3] Jaquerod and Scheuer, *Mem. Soc. Phys. Nat.*, 1908, p. 35.

[4] *Proc. Roy. Soc.*, 1910, Vol. A **83**, p. 414.

[5] Schwarz, *Ann. Physik.*, 1903, Vol. **11**, p. 303.

[6] *Proc. Roy. Soc.*, 1901, Vol **67**, p. 331.

[7] *Ann. Physikal*, 1910, Vol. **6**, p. 302.

[8] *Proc. Roy. Soc.*, 1903, Vol. **72**, p. 204; Vol. **73**, p. 346.

to radioactive material in the earth's crust, but such an explanation is not satisfactory for the large amounts of helium present in natural gas found in certain localities in the United States. It would take immense quantities of radium, uranium, or thorium to give rise to the large volumes of helium contained in these gases, and some other explanation is necessary. It has been shown that if the velocity of the alpha particle (helium atom) in radioactive changes were to fall below a certain value, the alpha particle would not be able to ionize gases and, therefore, its presence could not be detected by ordinary analytical radioactive methods.[1] In other words, an element might be radioactive in so far as disintegration and the elimination of alpha particles is concerned without our being able to detect this fact. If this is true, it would give at least a reasonable explanation of the presence of helium in such quantities in natural gas.

Liquefaction of Helium.—After several attempts by others, helium was successfully liquefied by Onnes. This was accomplished by the use of the Joule-Thompson effect after the gas had been pre-cooled by liquid hydrogen. The gas was circulated through an apparatus in which it was cooled first to the temperature of liquid air and then to −258°C. by means of liquid hydrogen boiling under reduced pressure. It was then liquefied in an apparatus using the general principles of the Hampson type of machine. Liquid helium is colorless and very mobile; its density is 0.154, and its maximum density is at about 2° absolute.[2] The boiling-point is 4.3° absolute; the critical temperature 5.25° absolute[3] and the critical pressure is 2.26 atmospheres. The critical volume (calculated) is 0.00271.

Commercial Manufacture of Helium.—In the fall of 1917, it was decided by the United States Army and Navy to attempt to extract helium in commercial quantities from the natural-gas wells at Petrolia, Tex., to be used in dirigibles and war balloons instead of hydrogen, as helium is non-inflammable and has many other advantages. A sufficient amount of money for experimental purposes was allotted from Army and Navy appropriations to the United States Bureau of Mines, which took charge of the work. Two experimental units were constructed at Fort Worth, Tex., connecting up with the gas supply at Petrolia by means of a pipe line. The plants at Fort Worth were an Air Reduction (Claude process) and a Linde Air Products plant (Linde Process). A third plant, using the Jefferies-Norton process, was constructed at Petrolia, Tex., at the source of supply of the gas. The natural gas at Petrolia carries about 36 per cent nitrogen and 60 per cent methane, in addition to small quantities of heavier hydrocarbons, such as ethane, propane, butane, etc. The problem calls for the successive liquefaction and fractionation of the hydrocarbons in the gas, and also of the nitrogen. Although the helium does not liquefy at the temperature involved, namely, that of liquid nitrogen, it is to a certain extent soluble in the liquefied gases, and as it is present in the proportion of only 0.93 per cent., it is necessary thoroughly to fractionate the liquids so that too much helium will not be lost by solubility. The plants of the Air Reduction Company and Linde Company were regular oxygen or nitrogen units modified to meet the particular problem at hand. The most serious trouble was met with in keeping the tops of the columns sufficiently cool for the final liquefaction of the nitrogen. The grade of product obtained

[1] *Cf.* p. 879.
[2] ONNES: *Comm. Phys. Lab* Leyden, No. 119.
[3] ONNES, *Proc. K. Akad. Wetensch*, Amsterdam, 1911, Vol. 14, p 678.

varied from 20 per cent to 70 per cent helium. This gas was refined by a process which practically involved squeezing out the nitrogen by passing the gas through a condenser at a pressure of 1,000 lb. per square inch at the temperature of liquid nitrogen. In this manner, a final product containing about 92 per cent helium was obtained, and over 200,000 cu. ft. were manufactured during the experimental period.

A commercial unit costing $2,000,000, consisting of six large Linde units, was decided upon by the Government as the result of the experimental work. The Jefferies-Norton process at Petrolia involves the use of three expansion engines for refrigeration purposes, and a heat interchanger consisting of seven sections, in which the hydrocarbons are progressively liquefied. The original pressure of 300 lb. is held all through the still and interchanger, and the gas is expanded through the expansion engines only after it has passed through the still and has returned to the high-pressure outside sections of the interchanger, from whence it is expanded through the expansion engines back into the low-pressure sections. The same general principles in the stills are involved as regards the extraction of the helium, but the still of the Jefferies-Norton Company uses reflux coils, through which the liquids are throttled, instead of condensers as is the case in the Claude and Linde columns.

ARGON

Occurrence.—Argon is found widely distributed in nature. It exists in the atmosphere in the proportion of 0.941 per cent by volume, after water vapor, and carbon dioxide have been removed from the air, and 1.1845 per cent by volume of atmospheric nitrogen.[1] The proportion of argon in the air is constant, as samples taken from widely different localities show practically no variation in the argon content. Over the open sea, however, slightly higher proportions of argon have been found. It is found to a small extent in sea and river water, owing to its being dissolved with the air. Since argon is slightly more soluble than air itself, the proportion by volume in natural waters is slightly higher. It has been found in many mineral springs, among them being those of Bath and Buxton; the old sulphur well at Harrogate, England; Monte Irone, Albano; the Poretta baths, Bolognian Apennines; Maizières, Côte d'Or, etc. It is also present in certain natural gas in Kentucky, and in the helium-bearing gas at Petrolia, Tex. Only a few minerals yield argon on heating; the chief of these are malacone[2] and a mineral from Brazil described by Antropoff.[3] Both minerals contain zirconium in considerable quantities, and both are radioactive. The amount of argon present is probably too large to be derived from atmospheric sources and, therefore, there is at least a possibility that argon may also be a product of the disintegration of radioactive elements, although there is no direct proof of this statement. Argon has also been found in eliastite[4] and in a mineral carrying cerium from the South Caucasus.[5]

Recovery from the Atmosphere.—Argon is extracted from the atmosphere by passing air over metallic copper and a strongly heated mixture of metallic magnesium and lime. The absorption of nitrogen by magnesium alone is a very slow

[1] SCHLOESING, *Comp. rend.*, 1895, Vol. **121**, p. 605, KELLAS, *Proc Roy. Soc.*, 1896, Vol. **59**, p. 66.
[2] RAMSAY and TRAVERS, *Proc. Roy. Soc.*, 1897, Vol. **60**, p. 442.
[3] *Zeit. Elektrochem.*, 1908, Vol. **14**, p 585.
[4] LOCKYER, *Proc. Roy. Soc.*, 1896, Vol. **60**, p. 133.
[5] TSCHERNIK, *J. Russ. Phys. Chem. Soc.*, 1897, Vol. **29**, p. 291.

process, but when mixed with lime the absorption is rapid and complete. The air is first passed over soda lime and phosphorus pentoxide, and then through a copper tube in which the oxygen is absorbed. From this it goes through the magnesium-lime mixture, over heated copper oxide, and finally through other soda lime and pentoxide tubes. In order to have the absorption complete, some care is required. First the apparatus must be completely exhausted and must remain airtight. Connections may be made by antimony pressure tubing of small bore. Black and gray rubber do not stick tightly to the joints, and the apparatus is sure to leak. It is bettter to make glass joints wherever possible, and reserve the rubber for connections with the hard-glass tubes. The lime must be as free from carbonate as possible and, of course, perfectly dry. Before the air is passed through it, the magnesium-lime tube is strongly heated and soon turns black, owing to the glass being attacked by the magnesium. During this process carbon monoxide and hydrogen are formed in considerable quantities; the first by the reduction of the carbon dioxide obtained from the traces of carbon in the lime, and the second from the action of water vapor on the magnesium. These gases should be pumped off as fast as formed, and when the evolution is practically finished, air is slowly admitted to the apparatus. Traces of carbon monoxide and hydrogen formed during the actual experiment are oxidized by the copper oxide, and the products absorbed by the soda lime and pentoxide tubes.

When the nitrogen reaches the magnesium-lime tube, absorption is indicated by a sudden rise in temperature and the formation of a glowing ring at the rear end of the tube. Unless this ring is formed, absorption is not taking place. The glow gradually goes down the tube as the magnesium is used up, making it easy to know when to stop the experiment. If the apparatus leaks, small traces of air may be removed from the argon obtained by sparking with oxygen in presence of a strong solution of caustic soda. The excess of oxygen is then removed by means of phosphorus. For larger quantities of argon it is more convenient to use the method of Fisher and Ringe, according to which air is passed over a mixture of 90 per cent calcium carbide and 10 per cent calcium chloride heated to 800°C. In this case, the temperature is too high for glass, and iron tubes must be used. With a properly prepared apparatus, considerable quantities of argon may readily be made. The nitrogen and carbide give carbon and cyanamide. The oxygen and carbide give lime and carbon, while carbon dioxide and monoxide formed at the same time react with the carbide to give carbon. Argon can also be extracted from the atmosphere by the original sparking method of Lord Rayleigh, in which an inverted flask is used containing a strong solution of caustic soda. Through a two-hole rubber stopper and passing up through the solution are two glass tubes containing electrodes. The oxides of nitrogen formed by the sparking are absorbed by the caustic-soda solution. Argon is now made commercially from the atmosphere by using the ordinary refrigeration method for liquifying air. The fractionation column—either the Claude process or the Linde process is used—is adapted so that a fraction of the gas is taken off between the liquefied oxygen and the liquid nitrogen, as liquid argon has a boiling-point between liquid oxygen and liquid nitrogen. In this manner, a product containing about 80 per cent of argon is obtained. It is purified by chemical methods already described, and finally used in incandescent lamps instead of nitrogen. Liquid argon is colorless and transparent, and boils at $-$ 186.1°C. Its *density* at this temperature is 1.4046. If allowed to cool by means of its own evaporation it can be solidified to a white mass which melts at -188.9°C.

Physical Properties.—Argon is an odorless, colorless and tasteless gas. Its *density* is 19.95 (O = 16), and the weight of a normal liter of gas is 1.782 g. Its *atomic* and *molecular weights* are, therefore 39.9. The *critical constants* of argon are as follows: *Critical density*, 0.509g./c.c;[1] *critical pressure*, 47.996 atmospheres[2] and the *critical temperature*, −122.44°C.[3] The *vapor pressure* of solid argon is 411 mm. at −190.9°. The *triple point* of argon is −189.3°. The *molecular heat* of vaporization of the liquid is 12.92 cal. at −125.49°; 24.01 cal. at −140.8°, and 35 cal. at −183.06°. The *coefficient of expansion* of the gas is 0.003668.[4] Its *viscosity* is 1.2 times that of air.[5] Its *solubility in water* is four volumes per 100 volumes of water at ordinary temperatures.[6] The *refractivity* ($\mu - 1$) of argon is:

Wave length λ	$(\mu - 1) \times 10^7$
6,439	2,796
5,461	2,823
4,359	2,851

The gas has a low *dielectric cohesion*, namely, 38, which is about one-fifth that of air. The *sparking distance* is about 40 per cent greater in argon than in air under similar conditions. The gas is *diamagnetic*. The *thermal conductivity* is K = 0.00003894 at 0°C. The *specific heats* at constant pressure and constant volume at ordinary temperatures have not been determined, but they have been determined at higher temperatures, namely, over 1,300°C. Argon gives two sets of spectrum lines, depending upon the pressure the gas is subjected to. For the sake of convenience, the two sets are called the red and blue spectrum. With a spark-gap and Leyden jar the blue spectrum is given. The principal lines are as follows:

"RED" SPECTRUM OF ARGON

Wave-length	Intensity	Wave-length	Intensity	Wave-length	Intensity
7,066.60	7	4,272.30	8	4,182.00	7
6,964.80	8	4,266.43	8	4,164.30	7
5,607.44	8	4,259.49	9	4,158.72	10
4,510.85	7	4,200.80	10	4,044.56	8
4,348.11	8	4,198.16	10	3,949.11	8
4,345.32	7	4,191.84	10	3,834.77	8
4,333.71	8	4,190.84	7	3,567.79	7
4,300.25	8				

[1] CROMMELIN, *Proc. K. Akad. Wetensch*, Amsterdam, 1910, Vol. **13**. p. 607.
[2] CROMMELIN, *ibib.*, p. 54.
[3] CROMMELIN, *ibid*, p. 54.
[4] KUENEN and RANDALL, *Proc. Roy. Soc.*, 1895, Vol. **59**, p. 60.
[5] RAYLEIGH, *Proc. Roy. Soc.*, 1896, Vol. **59**, p. 198.
[6] RAYLEIGH and RAMSAY, *Phil. Trans.*, 1895, Vol. **186**, p. 187.

"BLUE" SPECTRUM OF ARGON

Wave-length	Intensity	Wave-length	Intensity	Wave-length	Intensity
5,559.02	8	3,781.02	7	3,285.91	7
4,880.00	8	3,729.45	9	2,942 94	7
4,806 17	8	3,638.02	7	2,806 30	8
4,609.74	7	3,588 63	9	2,769 70	8
4,426 17	8	3,582 55	7	2,753 90	8
4,348 22	9	3,576.81	8	2,744 90	8
4,104.11	7	3,561.21	7	2,708 40	8
4,014 00	7	3,559.70	8	2,647 60	8
3,928.75	7	3,546 01	7	2,516.80	8
3,868.72	7	3,545 79	7	2,515.60	8
3,850.72	8	3,491 72	9		

NEON

Occurrence.—Neon is found terrestrially principally in the atmosphere. Watson's estimate is probably the most accurate, and his figure is one volume of neon in 55,000 volumes of air. Neon has been recognized in the gases from a number of thermal springs.[1] Recently, neon has also been detected in certain natural gases from Kansas and Texas, which also carry helium.

Separation.—Neon has usually been prepared by extracting the helium and neon together from the atmosphere and then separating these two gases either at the temperature of liquid hydrogen, at which temperature neon solidifies and the helium can be pumped off, or by fractionation from charcoal at liquid-air temperatures. A convenient method of getting a volume of nitrogen enriched with neon and helium is to take the gas escaping from an ordinary Hampson liquefying machine and return it to the intake of the compression pump. In this manner, the gas is partially liquefied and the more volatile constituents, namely, neon and helium, become concentrated in the gas given off. A somewhat similar result can be obtained by reliquefying all of the gas escaping from the air liquefier, and if a current of air is now brought through this liquid, the first portion that evaporates will be extremely rich in helium and neon.

The enriched gas must then be freed from nitrogen and traces of oxygen in the usual manner of passing over heated metallic copper to remove the oxygen, and over a heated mixture of magnesium and lime or over calcium carbide in order to remove the nitrogen. The mixture of neon and helium can be separated by means of liquid hydrogen, or more cheaply by fractionation from charcoal at the temperature of liquid air. In this latter process, the neon is more readily adsorbed by the charcoal than the helium, and it is possible to get a reasonably pure sample of neon in this manner. By means of a modification of his apparatus for the fractionation, condensation and distillation of liquid air, Claude has been able to obtain the neon, helium and hydrogen which exist in the air in considerable quantities. The gas thus obtained contains about 50 per cent nitrogen.[2]

[1] NOUREU and BIQUARD: *Compt. rend.*, 1906, Vol. **143**, p. 180; 1908, Vol. **146**, p. 435.
[2] CLAUDE, *Compt. rend.*, 1905, Vol. **141**, p. 823; 1908, Vol. **147**, p. 624.

Physical Properties.—The *absorption coefficient* of neon in water is 0.0114 at 0°C., and increases up to 0.0317 at 50°.[1] The *density* of the gas, according to Watson, is 10.08 (O = 16) the weight of a normal liter being 0.9002. The *atomic weight* is therefore 20.16. The *compressibility coefficient* at 0° between 0 and 1 atmosphere is −0.00105, and neon, therefore, like hydrogen is an ultra-perfect gas.[2] The *refractivity* of neon is 1.00006716 at 0° and 760 mm. for the green mercury line. The *dispersion at* N. P. T. is about twice that of helium. The *viscosity* of the gas at 0°C. is 2.981×10^{-4} in absolute units.[3] The *dielectric cohesion* of neon at 17° is 5.6; hydrogen being 205. The dielectric cohesion, therefore, is less than helium, whereas one would expect it to be between that of helium and argon. Very small traces of impurities raise the dielectric cohesion of neon considerably.

Liquefaction of Neon.—Neon can be liquefied and even solidified by means of liquid hydrogen. Its boiling-point is −245.92°C. Its *triple-point* pressure is 35 cm. of mercury, and its critical pressure is 29 atmospheres. According to Onnes and Crommelin[4] the *critical temperature* of neon is approximately 42° to 45° absolute. The *surface tension, density* and *refractive index* of liquid neon have not yet been measured, but it has been calculated that the *refractive index* should be about 1.24.

Spectrum.—Neon has a very characteristic spectrum, the most prominent visual lines being in the red and yellow. The wave lengths of the more prominent lines are as follows:

Wave-length	Intensity	Wave-length	Intensity	Wave-length	Intensity
6,402.40	10	6,183.79	10	5,974.73	6
6,383.15	8	6,143.28	10	5,944.91	10
6,328.38	6	6,128.63	8	5,882 04	8
6,304 99	8	6,096.37	10	5,852.65	20
6,266.66	10	6,074.52	10	5,764.54	8
6,217.50	8	6,030 20	10	4,259.53	6
6,182.37	10	5,975.78	8		

KRYPTON

Occurrence.—Krypton occurs in the atmosphere in the proportion of 1 part by volume in 20,000,000.[5] It has been found spectroscopically to exist in certain mineral springs, and also in certain natural gases in Kansas and Texas.

Separation.—Krypton has only been made in quantity once, and this was by Moore.[6] The oxygen residues obtained in a Claude air liquefying plant were used after about 100 tons of air had passed through the plant. The 50 l. of liquid oxygen left were allowed to evaporate slowly from Dewar flasks; the gas passing through a glass spiral dipping in liquid air. In this manner the oxygen and traces

[1] ANTROPOFF: *Proc. Roy. Soc*, 1910, Vol. A **83**, p. 474.
[2] BURT, *Trans. Faraday Soc.*, 1910, Vol. **6**, p. 19.
[3] RANKINE, *Proc. Roy. Soc.*, 1910, Vol. A **83**, p. 516, Vol. A **84**, p. 181.
[4] *Proc. K. Akad. Wetensch*, Amsterdam, 1915, Vol. **18**, p. 15, 1911, Vol. **14**, p. 163.
[5] RAMSAY, *Proc. Roy. Soc.*, 1903, Vol. **71**, p. 424; 1908, Vol. A **80**, p 599.
[6] *Trans. Chem. Soc.*, 1908, Vol. **93**, p. 2181; *Proc. Roy. Soc.*, 1908, Vol. A **81**, 195.

of nitrogen were not liquefied, but the krypton and xenon contained in the liquid oxygen were solidified in the spiral. The spiral was then removed from the liquid air, and the gases thus obtained collected over mercury and fractionated from each other. This is possible since the vapor pressure of krypton at the temperature of liquid air (17mm.) is nearly 10 times that of xenon.

Physical Properties.—Krypton is a colorless, odorless and tasteless gas. The *density* has been determined by Moore, using the best fractions obtained in the work described above. The value obtained was 41.506; oxygen being 16. The weight of a normal liter of krypton is, therefore, 3.708 g.[1] The *compressibility* of krypton was determined by Ramsay and Travers, and they showed that the value of *pv* decreases markedly with increase of pressure. Between 0 and 1 atmospheres, the *compressibility* is +0.00215. The *solubility* of krypton in water has been determined, the *absorption coefficient* is 0.1249 at 0°, 0.0788 at 20°, and 0.0823 at 50°. The *viscosity* at 10.6°C. is 1.361 times that of air; at 0° in absolute units, it is 2.344. Krypton is easily liquefied; it boils at −151.7°C. The *density* of the liquid at its boiling-point is 2.155. The *critical temperature* of the liquid is −62.5°C.; and its *critical pressure* is 54.3 atmospheres.[2] Krypton can easily be solidified, and the solid melts at −169°C. The *specific heat* of krypton has not been determined. The ratio of the specific heats was determined to be 1.689. Krypton undoubtedly has a monatomic molecule, and the *atomic weight* is, consequently, identical with the *molecular weight* and equals 82.92. This figure is based on Watson's theoretical correction of Moore's density determination.

Spectrum.—The spectrum of krypton depends materially upon the nature of the discharge. With the direct discharge in a Geissler tube, the number of lines is not large and is characterized mainly by a bright-green and a yellow line. When a spark-gap is used with a Leyden jar, a much larger number of lines show up in the blue. The aurora borealis gives a spectrum with a persistent green line which is probably the krypton green. The following represent the principal lines in the two spectra:

FIRST KRYPTON SPECTRUM (DIRECT DISCHARGE)

Wave-length	Intensity	Wave-length	Intensity
5,871 12	10	4,454.12	10
5,570 50*	10	4,400.11	6
5,562.45	6	4,376.33	10
4,671.40	10	4,362 83	9
4,624.48	10	4,319.76	10
4,502.56	9	4,318.74	8
4,501.13	7	4,274.15	10
4,463.88	10		

* Probably the green *auroral* line

[1] *Trans. Chem. Soc*, 1908, Vol. **93**, p. 2181.

[2] RAMSAY and TRAVERS, *Proc. Roy. Soc.*, 1901, Vol. **67**, p. 329; *Phil. Trans* 1901, Vol. **197**, p. 47.

SECOND KRYPTON SPECTRUM (CONDENSED DISCHARGE)

Wave-length	Intensity	Wave-length	Intensity
5,633.17[4]	6	4,109.38	6
4,765.90	6	4,098.89	7
4,739.16	7	4,088.48	8
4,619.31	6	4,065.22	8
4,577.40	6	4,057.17	8
4,475.18	7	3,994.98	6
4,355.67	10	3,920.29	8
4,293 10	6	3,917.76	6
4,145.28	6	3,906.37	8

XENON

Occurrence.—Xenon exists in the atmosphere to the extent of one volume in 190,000,000. It is also found to a very limited extent in the gases evolved from certain mineral springs[1] and also in certain natural gases from Kansas and Texas.

Separation.—Xenon has only been prepared in reasonable quantity on one occasion by R. B. Moore, as described under krypton.[2] From the oxygen residues obtained from 100 tons of liquid air, about 200 c.c. of pure xenon were finally obtained. Owing to the fact that the vapor pressure of xenon at the temperature of liquid air is very low, namely, 0.17 mm., its separation is greatly assisted. In fractionating xenon from krypton, the krypton can be gradually pumped off from the mixed solids since its vapor pressure is 10 times that of xenon. Finally a point is reached when the material seems to be pumped dry and no more krypton will come off. At this stage, it is necessary to warm up the gases and thus vaporize them, and then solidify them again by means of liquid air. A fresh surface is thus exposed, and a further small quantity of krypton can be pumped off. In this manner, pure xenon can be obtained.

Physical Properties.—It is a colorless, tasteless and odorless gas. Its *density* as determined by Moore,[3] is 65.35 (O = 16). Therefore, a normal liter of xenon weighs 5.815 g. Xenon is reasonably soluble in water; its *absorption coefficient* being 0.2189 at 0°C. and 0.0878 at 50°C. A minimum solubility occurs at about 40°C.[4] The *viscosity* of xenon at 0°C. is

$$N_0 = 2.107 \times 10^{-4},$$

while its *refractivity* is

$$\mu - 1 = 705.49 \times 10^{-6} \text{ for the green mercury line } (\lambda = 5461).$$

Xenon can be easily liquefied and solidified. The liquid is colorless and boils at −109.1°C. under atmospheric pressure. Its *density* at the boiling-point is 3.06 and, therefore, the molecular volume is 42.7. The *critical temperature* of xenon is +16.6°C., and the gas may be liquefied at this temperature by a pressure of

[1] MOUREU and LEPAPE, *Compt. rend.*, 1909, Vol. **149**, p. 1174.
[2] *Proc. Roy. Soc.*, 1908, Vol. A **81**, p. 195.
[3] *Trans. Chem. Soc.*, 1908, Vol. **93**, p. 2181; WATSON, *ibid.*, 1910, Vol. **97**, p. 833.
[4] ANTRAPOFF, *Proc. Roy. Soc.*, 1910, Vol. A **83**, p. 474.

58.2 atmospheres. The *melting-point* of solid xenon is −140°C. Its *atomic weight* is the same as its molecular weight, namely, 130.2 (O = 16).[1] The ratio of *specific heats* is 1.666.

Spectrum.—A Geissler tube containing xenon emits a blue line when a current is passed through it, and an examination of the spectrum shows that the principal lines are in the blue end of the spectrum. If a spark-gap and Leyden jar be used, the color of the tube changes to green. The following lists give the principal lines in the two spectra:

FIRST XENON SPECTRUM (UNCONDENSED DISCHARGE)

Wave-length	Intensity	Wave-length	Intensity	Wave-length	Intensity
4,923.28	6	4,624 46	15	4,116 25	7
4,916.63	6	4,582 89	5	4,109 84	5
4,807.19	6	4,524 83	6	4,078 94	10
4,734 30	8	4,501.13	10	3,967.74	10
4,697.17	7	4,193.70	8	3,951 16	10
4,671.42	10				

SECOND XENON SPECTRUM (CONDENSED DISCHARGE)

Wave-length	Intensity	Wave-length	Intensity	Wave-length	Intensity
6,097 80	7	4,921.68	6	4,415 00	7
6,051.36	7	4,883 68	6	4,406 99	5
6,036 40	6	4,876 68	7	4,395 91	10
5,976 67	7	4,862 69	8	4,393 34	10
5,719 83	6	4,844 50	10	4,330 63	15
5,667 85	6	4,823 47	6	4,245 54	10
5,616 99	6	4,652 15	6	4,238 37	10
5,531.33	7	4,603 21	10	4,208.61	6
5,472.90	7	4,592 22	6	4,193 25	8
5,460 63	6	4,585 65	10	4,180 20	10
5,439 19	8	4,577 36	6	4,109 20	6
5,419 40	10	4,545 34	8	4,050.19	6
5,372 62	8	4,541 03	8	3,950 70	8
5,339 56	9	4,481 01	7	3,922 67	10
5,314.15	8	4,462 38	20	3,908.00	7
5,292 40	10	4,448 28	10		
5,080 88	7	4,434 35	6		

RADIUM EMANATION

Niton.—The gas which is given off from radium as its first disintegration product has properties similar to those of the rare gases and is, therefore, often classed with these gases. The name, radium emanation, was given to the gas at the time of the first observation of its formation from radium, and was an excellent temporary name, but is not satisfactory at the present time, now that we know more

[1] MOORE, *Trans Chem. Soc*, 1908, Vol. **93**, p 2181.

about the gas and recognize it as an element, although a transition one. The name, niton (Nt), suggested by Sir William Ramsay, is an excellent one and at least as far as chemical usage goes should be adopted.

Occurrence.—Niton occurs in all minerals containing uranium and, therefore, in radium. As radium is widely distributed through the earth's crust and exists in minute quantities in all rocks and minerals, niton is an extremely widely disseminated element, although, owing to the fact that the quantities of radium in the earth's crust are small and to the fact that it decays rapidly, it exists only in almost infinitesimal quantities. The gas, therefore, occurs in the atmosphere, but the amount in a cubic meter of air is that which would be in equilibrium with 1×10^{-10} g. of radium.

Separation.—The only way by which niton can be obtained in anything like measurable quantities is from a high-grade radium salt. If such a salt is placed in water solution, the niton will accumulate, and after about 4 days approximately half the equilibrium amount will have been produced. At the same time a certain proportion of the water will be decomposed by the α rays into hydrogen and oxygen; there always being a slight excess of hydrogen, owing to the simultaneous formation of a small amount of hydrogen peroxide. If the gases are pumped off, the hydrogen and oxygen can be caused to recombine to form water, and the excess of hydrogen can be oxidized by means of heated copper oxide. Traces of carbon dioxide can be absorbed by solid caustic soda, and in this manner the niton can be purified and run into a small capillary tube for experiment, or observation. The volume of gas obtained, even under these favorable conditions, is small, as the amount that is in equilibrium with 1 g. of radium element is 0.585 cu. mm. at N.P.T.

Physical Properties.—Niton obeys all of the gas laws and can be manipulated like any other gas. Its *density* was determined by Ramsay and Gray[1] by weighing on a microbalance sensitive to 2×10^{-6} mg. The amount of emanation used was not more than 0.005 cu. mm. The mean of several experiments gave the value 111.5 (H = 1), which gives 223 as the *atomic weight of* niton. The gas is soluble in water; its *absorption coefficient* being approximately 0.5 at 0°; 0.3 at 15°; 0.27 at 18°; 0.23 at 20°; and 0.15 at 40°. No work has been done on the *specific heats* of niton, but from analogy with the rare gases, it is assumed that it is monatomic. The gas is easily liquefied and frozen. Its *critical temperature* is 104.5°, and its *critical pressure* is 62.5 atmospheres. Niton boils at −62°, and freezes at −71°C. Its vapor pressure at −71°C. is 500 mm. Its heat evolution (including disintegration products up to Ra C) is about 106 g. calories per hour for the emanation in equilibrium with 1 g. of radium.

Spectrum.—When placed in a capillary tube and an electrical discharge is passed through the gas, niton gives a spectrum which does not vary with the character of the discharge. Ramsay and Collie[2] first examined the spectrum visually and noticed a strong and persistent line at $\lambda = 5{,}595$. Since that time the spectrum has been mapped in more detail by other observers.[3]

[1] *Proc. Roy. Soc.*, 1911, Vol. **84**, p. 536.

[2] *Proc. Roy. Soc.*, 1914, Vol. **73**, p. 470.

[3] WATSON: *Proc. Roy. Soc.*, 1909, Vol. A **83**, p. 50; RAMSAY and CAMERON: *Proc. Roy. Soc.*, 1908, Vol. A **81**, p. 210; RUTHERFORD and ROYDS: *Phil. Mag.*, 1908, Vol. **16**, p. 313; ROYDS: *Phil. Mag.*, 1909, Vol. **17**, p. 202.

SECTION XXIX

MATERIALS OF CONSTRUCTION

By Percy E. Barbour[1]

Introduction.—The general design of plants is considered in Section XXX, so that this Section is merely a discussion of the properties of materials, without consideration of what is to be done with them. Further information, both as to the properties of materials in the abstract, and as to their use in structures may be found in: Kidder's "Architects and Builder's Pocket Book," M. S. Ketchum's "Steel Mill Buildings" H. G. Tyrrell's "Engineering of Shops and Factories;" Day's "Industrial Plants (*N. Y. Eng. Mag.*); Dyson & Clarkson's "Chemical Works" (Scott, Greenwood & Son, London and Van Nostrand, New York); Charnock's "Mechanical Technology" (Constable & Co., London); Knott & Mackay's "Practical Mathematics" (W. & R. Chambers, Edinburgh, Van Nostrand, New York).

Iron and Steel.—The following definitions were adopted by the Committee on the Uniform Nomenclature of Iron and Steel of the International Association for Testing Materials, September 1906.

Cast Iron.—Iron containing so much carbon or its equivalent that it is not malleable at any temperature. The committee recommends drawing the line between cast iron and steel at 2.20 per cent carbon.

Pig Iron.—Cast iron which has been cast into pigs direct from the blast furnace.

Bessemer Pig Iron.—Iron which contains so little phosphorus and sulphur that it can be used for conversion into steel by the original or acid bessemer process restricted to pig iron containing not more th n 0.10 per cent of phosphorus.

Basic Pig Iron.—Pig iron containing so little silicon and sulphur that it is suited for easy conversion into steel by the basic open-hearth process (restricted to pig iron containing not more than 1.00 per cent of silicon).

Gray Pig Iron and Gray Cast Iron.—Pig iron and cast iron in the fracture of which the iron itself is nearly or quite concealed by graphite, so that the fracture has the gray color of graphite.

White Pig Iron and White Cast Iron.—Pig iron and cast iron in the fracture of which little or no graphite is visible, so that the fracture is silvery and white.

Malleable Castings.—Castings made from iron which when first made is in the condition of cast iron, and is made malleable by subsequent treatment without fusion.

Malleable Pig Iron.—An American trade name for pig iron suitable for converting into malleable castings through the process of melting, treating when molten, casting in a brittle state, and then making malleable without remelting.

Wrought Iron.—Slag-bearing, malleable iron, which does not harden materially when suddenly cooled.

Steel.—Iron which is malleable at least in some one range of temperature and in

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addition is either (*a*) cast into an initially malleable mass; or, (*b*) is capable of hardening greatly by sudden cooling; or, (*c*) is both so cast and so capable of hardening.

Openhearth Steel.—Steel made by the openhearth process, irrespective of carbon content.

Bessemer Steel.—Steel made by the bessemer process, irrespective of carbon content.

Blister Steel.—Steel made by carburizing wrought iron by heating it in contact with carbonaceous matter.

Crucible Steel.—Steel made by the crucible process, irrespective of carbon content.

Steel Castings.—Unforged and unrolled castings made of bessemer, openhearth, crucible or any other steel.

Alloy Steels.—Steels which owe their properties chiefly to the presence of an element other than carbon.

Classification of Iron and Steel.—The limits of carbon, the specific gravity and properties of iron and steel are as follows:

	Per cent of Carbon	Specific Gravity	Properties
Cast iron	5 to 1.50	7.2	Not malleable, not temperable
Steel	1.50 to 0.10	7.8	Malleable, and temperable
Wrought iron	0.30 to 0.05	7.7	Malleable, not temperable

It will be seen that the percentage of carbon alone is not sufficient to distinguish between steel and wrought iron. The softer grades of steel resemble wrought iron. Very mild openhearth steel is often sold under the trade name of "ingot iron," and is reputed to have many advantages over structural steel, some of which are questionable.

Cast Iron.—The product of the blast furnace, where the iron ore is reduced in the presence of a flux, is called pig iron. The term cast iron is commonly applied to pig iron after it has been again melted and cast into finished form. Cast iron contains carbon, silicon, sulphur, phosphorus and manganese in addition to pure iron, and occasionally very small quantities of other elements.

Carbon.—The percentage of carbon ordinarily varies between 1½ and 4 per cent, but in the presence of manganese the carbon may be much higher. Carbon may occur in the form of combined carbon, giving a white brittle cast iron, or in the form of graphite, giving a gray cast iron, which is the form used in structural castings. The proper amount of carbon in cast iron depends upon the amount of other impurities and upon the use that is to be made of the finished product.

Silicon.—The carbon is controlled by varying the amount of silicon and sulphur. Silicon acts as a precipitant of carbon, changing it from the combined form to the graphite form. The silicon in gray cast iron is usually between ¾ and 3 per cent.

Sulphur.—Sulphur has the opposite effect of silicon and its presence is considered objectionable. Sulphur produces "red-shortness" (brittleness when the iron is heated). The amount of sulphur in gray-iron castings should not exceed 0.12 per cent.

Manganese.—Manganese and sulphur both tend to increase the amount of combined carbon, but they tend to neutralize each other. Manganese gives closeness of grain and prevents the absorption of sulphur on remelting. The amount of manganese in gray-iron castings is usually less than ½ per cent; more than 2 per cent makes cast iron brittle.

Phosphorus.—Phosphorus increases the fusibility and fluidity of cast iron but at the same time makes it brittle. A high phosphorus content is necessary in cast iron

for light ornamental castings where strength is not required. The phosphorus in gray-iron castings varies from ½ to 1½ per cent.

Nickel steel for structural purposes is made by the openhearth process and conforms to the following requirements as to chemical composition in terms of per cent.:

	Structural steel	Rivet steel
Carbon	not over 0 45	not over 0.30
Manganese	not over 0.70	not over 0.60
Phosphorus, Acid	not over 0.05	not over 0.04
Phosphorus, Basic	not over 0.04	not over 0.03
Sulphur	not over 0 05	not over 0.045
Nickel	not under 3.25	not under 3.25

The material has a tensile strength of 70,000 to 80,000 lb. per square inch for rivet steel and 85,000 to 100,000 lb. per square inch for plates, shapes and bars.

Structural steel may be made by the bessemer or the openhearth process except that rivet steel and steel for plates or angles over ¾ in. in thickness which are to be punched shall be made by the openhearth process. Structural steel to meet these standard specifications must conform to the following requirements as to chemical composition:

	Structural steel, per cent	Rivet steel, per cent
Phosphorus bessemer	not over 0.10	
Openhearth	not over 0 06	not over 0.06
Sulphur		not over 0.045

Structural steel has a tensile strength of 55,000 to 65,000 lb. per square inch and rivet steel 46,000 to 56,000 lb. per square inch.

When steel plates for structural purposes are ordered to gage, the thickness of each plate shall not vary more than 0.01 in. under that ordered. One cubic inch of rolled steel is assumed to weigh 0.2833 lb.

Malleable Castings.—Small thin castings made of white cast iron may be decarbonized by heating the castings in annealing pots containing hematite ore or forge iron scale. The castings are kept at a cherry red heat for 3 to 4 days, and are then allowed to cool slowly. The metal in malleable castings should not exceed ¼ in. in thickness in small castings, nor ½ in. in large castings, and should be of uniform thickness.

Steel for concrete reinforcement bars may be made by bessemer or the openhearth process. Bars shall be rolled from new billets only and shall conform to the following chemical compositions:

Phosphorus	Bessemer	not over 0.10 per cent
	Openhearth	not over 0.05 per cent

Carbon Steel Forgings.—Carbon steel for welding and case hardening Class A and for case hardening when subsequently heat treated Class B must conform to the following requirements as to chemical composition:

	Class A	Class B
Carbon, per cent	0.08 to 0.18	0.15 to 0.25
Manganese, per cent	0.30 to 0.50	0.30 to 0.50
Phosphorus maximum, per cent	0.045	0.045
Sulphur maximum, per cent	0.05	0.05

Refined wrought iron bars shall be made wholly from puddled iron and may consist either of new muck-bar iron or a mixture of muck-bar iron and scrap but shall be free from any admixture of steel. The iron shall have a tensile strength of 48,000 lb. per square inch.

Lake Copper.—In order to be classed as Lake, copper must originate on the northern peninsula of Michigan, and may be furnished in wire bars, cakes, slabs, billets, ingot bars, or ingots. Lake copper offered for electrical purposes, whether fire or electrolytically refined shall be known as "low-resistance lake." Low-resistance Lake wire bars shall have a resistivity not to exceed 0.15535 international ohms per meter-gram at 20°C. (annealed). All ingots and ingot bars shall have a resistivity not to exceed 0.15694 international ohms per meter-gram at 20°C. (annealed).

Lake copper having a resistivity greater than 0.15694 international ohms per meter-gram at 20°C. (annealed) shall be known as "high-resistance Lake." Low-resistance Lake copper shall have a purity of at least 99.880 per cent as determined by electrolytic assay, silver being counted as copper. High-resistance Lake copper shall have a purity of at least 99.880 per cent, copper, silver, and arsenic being counted together. The arsenic content of high-resistance Lake copper for special purposes shall be subject to agreement at time of purchase.

Electrolytic Copper.—Electrolytic-copper wire bars, cakes, slabs, billets, ingots, and ingot bars shall have a purity of at least 99.880 per cent as determined by electrolytic assay, silver being counted as copper. All wire bars shall have a resistivity not to exceed 0.15535 international ohms per meter-gram at 20°C. (annealed); all ingot and ingot bars shall have a resistivity not to exceed 0.15694 international ohms per meter-gram at 20°C. (annealed). Cakes, slabs, and billets shall come under the ingot classification except when specified for electrical use at time of purchase, in which case wire bar classification will apply.

Spelter.—Under the standard specifications of the A. S. T. M., virgin spelter is the zinc product resulting from ore or similar raw material by reduction and distillation and not produced from re-worked metal and is considered in four grades, as follows:

	Contains Not over				
	Pb	Fe	Cd	Al	Pb + Cd + Fe
A. High grade	0.07	0.03	0.07	0.0	0.10
B. Intermediate	0.20	0.03	0.50	0.0	0.50
C. Brass special	0.60	0.03	0.50	0 0	1.00
D. Prime Western	1.60	0.08	not specified		

Manganese Bronze.—The A. S. T. M. standard specification covers manganese-bronze ingots having notched flat bottoms, approximately 3 by 2¾ in.

wide by 12 in. long, properly tapered to strip easily from an iron mold. The chemical composition shall be as follows:

Copper	53 to 62 per cent
Zinc	36 to 54 per cent
Aluminum	0.05 to 0.5 per cent
Lead	not over 0.15 per cent

The ultimate tensile strength shall not be less than 70,000 lb. per square inch.

Corrugated steel is used for roofing and siding of many plants where the climatic conditions permit. It is too hot in hot countries for closed-in structures and too cold for cold countries. Corrugated steel is made from plain flat bessemer steel sheets by rolling in the corrugations one at a time. Iron and open-hearth steel corrugated sheets may be obtained but only with difficulty and extra cost. The standard corrugation is 2½ in. wide and ⅝ in. deep; special corrugations may be obtained at extra cost but like all special material is inadvisable if avoidable.

Corrugated steel may be either plain black unpainted, galvanized or covered with a coating of asbestos material, lead, etc. Plain black must be painted before and also after erection to prevent rusting and corrosion. Galvanized does not take paint readily unless washed with weak acid.

The standard width of corrugated sheets is 26 in. after corrugating. It is laid with either one or two corrugations side lap depending upon climatic and other conditions incident to the use of the building. When laid with one lap a sheet will cover a width of 24 in. and with two laps will cover 21½ in. in width. Endwise the lap should be 6 in. for roofing and 4 in. for siding. The United States standard gage is used for specifying thickness and weight. Amounts of corrugated steel are specified in squares 10 by 10 ft. or 100 sq. ft. The weights of different gages, in general use, per square (100 sq. ft.) for standard sheets with 2½ in. by ⅝ in., corrugations are given in the table below, no allowances being made for laps.

WEIGHT OF FLAT, AND CORRUGATED STEEL SHEETS WITH 2½-IN. CORRUGATIONS. WEIGHT PER SQUARE (100 SQ. FT.)

Gage No.	Thickness in inches	Flat sheets		Corrugated sheets	
		Black	Galvanized	Black painted	Galvanized
16	0.0625	250	266	275	291
18	0.0500	200	216	220	236
20	0.0375	150	166	165	182
22	0.0313	125	141	138	154
24	0.0250	100	116	111	127
26	0.0188	75	91	84	99
28	0.0156	63	79	69	86

Trautwine allows about one seventh more weight per square for side lap of one corrugation and end lap of 4 in. Standard stock lengths of corrugated vary by 6-in.

differences and run from 5 ft. to 10 ft. long. Odd lengths may be obtained at extra cost and generally with extra delay.

Corrugated Steel Fastenings.—Corrugated steel is fastened to wooden sheathing, girts, nailing strips, or purlins with barbed roofing nails; 8 d. nails 2½ in. long being commonly used spaced 6 to 8 in. apart. For estimating, 100 nails per square of corrugated covering is used.

For fastening corrugated to angle or channel girts or purlins without wooden nailing strips clinch nails are used made of ⅛ in. No. 10 soft-iron wire with flat head and are clinched around the steel member.

TABLE OF CLINCH NAILS

∠. Purlin leg.....	3 inches	4 inches	5 inches	6 inches	7 inches
Length.....	5 inches	6 inches	7 inches	8 inches	9 inches
No. per pound.....	32	29	23	21	18
[. Purlin leg	3 inches	4 inches	5 inches	6 inches	7 inches
Length.....	6 inches	7 or 8 inches	9 inches	10 inches	11 inches
No. per pound.....	29	21	18	16	14

NUMBER OF BARBED ROOFING NAILS IN 1 LB.

Size	Length, inches	Gage No.	Number in 1 lb.	Size	Length, inches	Gage No.	Number in 1 lb.
4 d.	1½	13	339	20 d.	4	6	30
6 d.	2	12	205	30 d.	4½	5	23
8 d.	2½	10	96	40 d.	5	4	17
10 d.	3	9	63	50 d.	5½	3	13
12 d.	3½	8	52	60 d.	6	2	10
16 d.	3½	7	38				

Holes for nails are punched in the top of the corrugations. Side laps may be riveted with copper rivets to make a tight job. Corrugated may also be fastened by metal straps around the supporting members riveted to the corrugated.

The safe load for corrugated steel sheets may be obtained from trade catalogues or computed by Rankine's formula

$$W = \frac{4}{15}\sqrt{\frac{Shbt}{l}}$$

Where, W = safe load in pounds;
S = working stress in pounds;
h = depth of the corrugations in inches;
b = width of the sheet in inches;
t = thickness of the sheet in inches;
l = clear span in inches.

The "Carnegie Handbook" gives the following formula for transverse strength of corrugated.

$$W = \frac{49.95\,tbd}{l}$$

$$w = \frac{99{,}900\,tbd}{l}$$

l = unsupported length of sheet in inches.
t = thickness of sheet in inches.
b = width of sheet in inches.
d = depth of corrugations in inches.
W = breaking weight distributed in tons.
w = breaking weight distributed in lbs.

Corrugated steel of 24 gage and lighter is seldom used, it being too thin to stand service and corrosion. Roofing is generally used a gage or two heavier than siding in the same structure because of the increased severity of service conditions.

Sulphurous gases from coal or smelting operations are particularly corrosive to galvanized or plain-black corrugated; lead or oxide paints afford little protection. Asphaltum or graphite paints should be used.

Anti-condensation lining. Where corrugated roofing is used in a heated building moisture will collect and considerable dripping may result. To obviate this chicken wire is stretched from eaves to ridge and covered with paper or asbestos and then felt and the corrugated is then laid on top in the usual way.

Protection of Iron and Steel against Corrosion.—If iron and steel are left unprotected to the atmosphere or to water they will corrode by rusting. Rust is ferric hydroxide, approximating FeO_3H_3. Dry air or water free from oxygen has no effect on iron or steel. Acids greatly hasten corrosion though not essential to it. Where iron and steel are in contact with water an electrolytic action always takes place and where the electrolytic force is considerable the corrosion is greatly increased. Covering iron or steel with a protective coating not acted on by air or water will retard or prevent corrosion. Cast iron owing to its carbon content and the silicon coating from its molding rusts much more slowly than steel or wrought iron.

The ordinary method of protecting iron and steel is by paints, of which there are many kinds, the most common being oil, tar and asphaltum paints.

An oil paint consists of a drying oil and a pigment thoroughly mixed that will be workable and is readily applied, has good covering powers, adheres to the metal and is durable. Linseed oil is commonly used and is unsurpassed in durability. The pigments used in making oil paints for protecting metal are lead, zinc, iron and carbon.

Raw linseed oil, made from crushing and pressing flaxseed, dries very slowly and is not often used in the pure state for structural paints. It is made to dry more rapidly by boiling or by adding a drier. Driers are made in various ways, the usual ones being fatty salts of those metals having more than one common valence, such as iron, manganese, etc., and the more drier is added the quicker the paint will dry and the poorer it becomes.

White lead (hydrated carbonate of lead) is the best white oil paint for interior and exterior wood work, has good adhesion and covering quality but is readily acted on by corrosive gases, turns dark and disintegrates. Is not a good paint to use on metal except over another paint.

Red lead (lead tetroxide) is the most commonly used paint for the first protective coating of steel for structural, bridge, ship and other purposes. It is stable and durable under all weather conditions. One ounce of lampblack added to one pound of red lead gives a deep chocolate color and lengthens the time of drying.

Zinc white (zinc oxide) is a white powder used for paint which has a good covering quality; used alone it has a tendency to peel and to deteriorate and wash off. Mixed with lead, however, and ground in linseed oil it forms a very durable paint for metallic surfaces.

Iron oxide is used frequently for red paint for wooden buildings but is not a good paint for metal. It is composed of anhydrous sesquioxide (hematite) and hydrated sesquioxide of iron which is iron rust. It hastens corrosion when applied to structural steel.

Carbon in the form of lampblack and graphite is much used for black paints. Lampblack in oil makes an excellent paint, the oil absorbing the carbon. Graphite is not absorbed by oil but forms a good paint the particles being held together by cementing action. The Dixon Graphite Co. of Jersey City uses a flake graphite combined with silica, while the Detroit Graphite Manufacturing Co. uses a mineral ore with a large percentage of graphite carbon in granulated form. Graphite paints have a large covering capacity.

Asphalt paint is a mixture of coal tar or mineral asphalt combined with a mineral base or oil. Various trade brands are purchasable of various combinations. Black Bridge paint made by Edward Smith & Co., New York, contains asphaltum, linseed oil, turpentine and Kauri gum. Asphalt paints are very satisfactory for metal.

Coal tar is often used for painting iron work. It should be free from acid and should be applied hot. It will run in hot weather, so is not a good paint for many purposes but where this can be obviated by local conditions finds much use. Oil paint will not stick to tar paint and the latter must first be removed before an oil paint is applied.

Ketchum quotes from the "Pencoyd Handbook" the following table for the covering capacity of paints:

AVERAGE SURFACE COVERED PER GALLON OF PAINT

Paint	Volume of oil, gallons	Pounds of pigment	Volume and weight of paint	Square feet	
				One coat	Two coats
			Gallons Pounds		
Iron oxide (powdered)....	1	8.00	1.2 = 16.00	600	350
Iron oxide (ground in oil)..	1	24.75	2.6 = 32.75	630	375
Red lead (powdered).....	1	22.40	1.4 = 30.40	630	375
White lead (ground in oil)..	1	25.00	1.7 = 33.00	500	300
Graphite (ground in oil)...	1	12.50	2.0 = 20 50	630	350
Black asphalt.....	1 (turpentine)	17.25	4.0 = 30.00	515	310
Linseed oil (no pigment)....	1			875	

Ketchum gives ½ gal. for first coat and ⅜ gal. for second coat per ton of structural steel as average paint required under average conditions, light structural steel averaging 250 sq. ft. and heavy structural steel about 150 sq. ft. per ton of metal.

STRUCTURAL TIMBER

The term "Structural Timber" was defined by the A. S. T. M. Committee as all such products of wood in which the strength of the timber is the controlling element in their selection and use. The following is a list of products which are recommended for consideration as structural timbers: Trestle timbers—

stringers, caps, posts, mud sills, bracing, bridge ties, guard rails; Car timbers—car framing, including upper framing; car sills; Framing for buildings—posts, mud sills, girders, framing, joists; Ship timbers—ship timbers, ship decking; Cross arms for poles.

Standard Defects.—Measurements which refer to the diameter of knots or holes should be considered as referring to the mean or average diameter

1. *Sound Knot.*—A sound knot is one which is solid across its face and which is as hard as the wood surrounding it; it may be either red or black, and is so fixed by growth or position that it will retain its place in the piece.

2. *Loose Knot.*—A loose knot is one not firmly held in place by growth or position.

3. *Pith Knot.*—A pith knot is a sound knot with a pith hole not more than ¼ in. in diameter in the center.

4. *Encased Knot.*—An encased knot is one whose growth rings are not intergrown and homogeneous with the growth rings of the piece it is in. The encasement may be partial or complete; if intergrown partially or so fixed by growth or position that it will retain its place in the piece, it shall be considered a sound knot; if completely intergrown on one face, it is a water tight knot.

5. *Rotten Knot.*—A rotten knot is one not as hard as the wood it is in.

6. *Pin Knot.*—A pin knot is a sound knot not over ½ in. in diameter.

7. *Standard Knot.*—A standard knot is a sound knot not over 1½ in. in diameter.

8. *Large Knot.*—A large knot is a sound knot, more than 1½ in. in diameter.

9. *Round Knot.*—A round knot is one which is oval or circular in form.

10. *Spike Knot.*—A spike knot is one sawn in a lengthwise direction; the mean or average width shall be considered in measuring these knots.

11. *Pitch Pockets.*—Pitch pockets are openings between the grain of the wood containing more or less pitch or bark. These shall be classified as small, standard, and large pitch pockets. (*a*) A small pitch pocket is one not over ⅛ in. wide. (*b*) A standard pitch pocket is one not over ⅜ in. wide, or 3 in. in length. (*c*) A large pitch pocket is one over ⅜ in. wide, or over 3 in. in length.

12. *Pitch Streak.*—A pitch streak is a well-defined accumulation of pitch at one point in the piece. When not sufficient to develop a well-defined streak, or where the fiber between grains, that is, the coarse-grained fiber, usually termed "spring wood," is not saturated with pitch, it shall not be considered a defect.

13. *Wane.*—Wane is bark, or the lack of wood from any cause, on edges of timbers.

14. *Shakes.*—Shakes are splits or checks in timbers which usually cause a separation of the wood between annual rings.

15. *Rot, Dote and Red Heart.*—Any form of decay which may be evident either as a dark-red discoloration not found in the sound wood, or the presence of white or red rotten spots, shall be considered as a defect.

16. *Ring Shake.*—An opening between the annual rings.

17. *Through Shake.*—A shake which extends between two faces of a timber.

Standard Names for Structural Timbers.—1. Southern Yellow Pine.—Under this heading two classes of timber are used: (*a*) Longleaf pine; (*b*) shortleaf pine. It is understood that these two terms are descriptive of quality, rather than of botanical species. Thus, shortleaf pine would cover such species as are now known as North Carolina pine, loblolly pine, and shortleaf pine. Longleaf pine is descriptive of quality, and if Cuban, shortleaf, or loblolly pine is grown under such conditions that it produces a large percentage of hard summer wood, so as to be equivalent to the wood produced by the true longleaf, it would be covered by the term longleaf pine.

AVERAGE ULTIMATE BREAKING UNIT STRESSES, IN POUNDS PER SQUARE INCH

Kind of timber	Tension		Compression			Transverse		Shearing	
			With grain						
	With grain	Across grain	End bearing	Columns under 15 diameters	Across grain	Extreme fiber stress	Modulus of elasticity	With grain	Across grain
White oak	12,000	2,000	7,000	5,000	2,000	7,000	1,500,000	800	4,000
White pine	7,000	500	5,500	3,500	700	4,000	1,000,000	400	2,000
Southern long-leaf or Georgia yellow pine	12,000	600	7,000	5,000	1,400	7,000	1,500,000	600	5,000
Douglas fir	8,000		5,700	4,500	800	5,000	1,400,000	500	
Short-leaf yellow pine	9,000	500	6,000	4,500	1,000	6,000	1,200,000	400	4,000
Red pine (Norway pine)	8,000	500	5,000	4,000	800	5,000	1,130,000		
Spruce and eastern fir	8,000	500	6,000	4,000	700	4,000	1,200,000	400	3,000
Hemlock	6,000			4,000	600	3,500	900,000	350	2,500
Cypress	6,000		5,000	4,000	700	5,000	900,000		
Cedar	7,000		5,500	3,500	700	4,000	700,000	400	1,500
Chestnut	8,500			4,000	900	5,000	1,000,000	600	2,000
California redwood	7,000			4,000	600	4,500	700,000	400	
California spruce				4,000		5,000	1,200,000		

AVERAGE SAFE ALLOWABLE WORKING UNIT STRESSES, IN POUNDS PER SQUARE INCH

Kind of timber	Tension		Compression			Transverse		Shearing	
			With grain						
	With grain	Across grain	End bearing	Columns under 15 diameters	Across grain	Extreme fiber stress	Modulus of elasticity	With grain	Across grain
Factor of Safety	Ten	Ten	Five	Five	Four	Six	Two	Four	Four
White oak	1,200	200	1,400	1,000	500	1,200	750,000	200	1,000
White pine	700	50	1,100	700	200	700	500,000	100	500
Southern long-leaf or Georgia yellow pine	1,200	60	1,400	1,000	350	1,200	750,000	150	1,250
Douglas fir	800		1,100	900	200	800	750,000	130	
Short-leaf yellow pine	900	50	1,200	900	250	1,000	600,000	100	1,000
Red pine (Norway pine)	800	50	1,000	800	200	800	565,000		
Spruce and eastern fir	800	50	1,200	800	200	700	600,000	100	750
Hemlock	600	...		800	150	600	450,000	100	600
Cypress	600	...	1,000	800	200	800	450,000		
Cedar	700	...	1,100	700	200	700	350,000	100	400
Chestnut	850	...		800	250	800	500,000	150	500
California redwood	700	...		800	150	750	350,000	100	
California spruce		...		800	...	800	600,000		

The above tables are based on those recommended by the committee on "Strength of Bridge and Trestle Timbers" of the Association of Railway Superintendents of Bridges and Buildings at their Fifth Annual Convention in October, 1895, but the arrangement and values in many cases are now modified by later data from various sources.

2. *Douglas Fir.*—The term Douglas fir is to cover the timber known likewise as yellow fir, red fir, western fir, Washington fir, Oregon or Puget Sound fir or pine, northwest and west coast fir.

3. *Norway Pine,* to cover what is known also as red pine.

4. *Hemlock,* to cover Southern or Eastern hemlock; that is, hemlock from all States east of and including Minnesota.

5. *Western hemlock,* to cover hemlock from the Pacific coast.

6. *Spruce,* to cover Eastern spruce; that is, the spruce timber coming from points east of Minnesota.

7. *Western spruce,* to cover the spruce timber from the Pacific coast.

8. *White pine,* to cover the timber which has hitherto been known as white pine, from Maine, Michigan, Wisconsin and Minnesota.

9. *Idaho white pine,* the variety of white pine from western Montana, northern Idaho, and eastern Washington.

10. *Western pine,* to cover the timber sold as white pine coming from Arizona, California, New Mexico, Colorado, Oregon and Washington. This is the timber sometimes known as Western yellow pine, or Ponderosa pine, or California white pine, or western white pine.

11. *Western larch,* to cover the species of larch or tamarack from the Rocky Mountain and Pacific coast regions.

12. *Tamarack,* to cover the timber known as tamarack, or Eastern tamarack, from States east of and including Minnesota.

13. *Redwood,* to include the California wood usually known by that name.

Yellow-pine bridge and trestle timber specifications were defined by the A. S. T. M. in 1910 and revised in 1915. Except as noted, all timber shall be cut from sound trees and sawed to standard size, close-grained and solid, free from defects, such as injurious ring shakes and crooked grain, unsound or loose knots, knots in groups, decay, large pitch pockets or other defects that will materially impair its strength.

Standard Size of Sawed Timber.—Rough timbers sawed to standard size shall mean that they shall not be over ¼ in. scant from the actual size specified. For instance, a 12 by 12-in. timber shall measure not less than 11¾ by 11¾ in.

Standard Dressing of Sawed Timber.—Standard dressing shall mean that not more than ¼ in. shall be allowed for dressing each surface. For instance, a 12 by 12-in. timber after being dressed on four sides shall measure not less than 11½ by 11½ in.

STONE

Stone.—Very few stones will withstand the action of severe heat which necessitates caution in their use in structures where fireproofing is required. Granite may explode or entirely disintegrate when subjected to severe heat. Limestones and marbles have little resistance in an ordinary fire. Sandstone will withstand more fire effect than any of the others but often after a severe conflagration will need to be replaced.

Kidder gives the following crushing strengths of stone and brick.

CRUSHING RESISTANCE OF BRICK, STONE, AND CONCRETES, (PRESSURE AT RIGHT ANGLES TO BED)

	Pounds per Sq. In.
Brick: Common, Massachusetts	10,000
Common, St. Louis	6,417
Common, Washington, D. C.	7,370
Paving, Illinois	6,000 to 13,000
Granites. Blue, Fox Island, Me.	14,875
Gray, Vinal Haven, Me	13,000 to 18,000
Westerly, R. I.	15,000
Rockport and Quincy, Mass	17,750
Milford, Conn	22,600
Staten Island, N. Y.	22,250
East St. Cloud, Minn.	28,000
Gunnison, Colo.	13,000
Red, Platte Cañon, Colo	14,600
Limestones: Glens Falls, N. Y.	11,475
Joliet, Ill	12,775
Bedford, Ind	6,000 to 10,000
Salem, Ind.	8,625
Red Wing, Minn.	23,000
Stillwater, Minn.	10,750
Sandstones: Dorchester, N. B. (brown)	9,150
Mary's Point, N. B. (fine grain, dark brown)	7,700
Connecticut brown stone,* on bed	7,000 to 13,000
Longmeadow, Mass. (reddish brown)	7,000 to 14,000
Longmeadow, Mass. average, for good quality	12,000
Little Falls, N. Y.	9,850
Medina, N. Y.	17,000
Potsdam, N. Y. (red)	18,000 to 42,000
Cleveland, Ohio	6,800
North Amherst, Ohio	6,212
Berea, Ohio	8,000 to 10,000
Hummelstown, Pa.	12,810
Fond du Lac, Minn.	8,750
Fond du Lac, Wis.	6,237
Manitou, Colo. (light red)	6,000 to 11,000
St. Vrain, Colo. (hard laminated)	11,505
Marbles: Lee, Mass.	22,900
Rutland, Vt.	10,746
Montgomery Co., Pa.	10,000
Colton, Cal.	17,783
Italy	12,156
Flagging: North River, N. Y.	13,425

* This stone should not be set on edge.

Fireproof Construction.—In modern structures fireproof floors and walls are a necessity. Such floors are made by using terracotta tile or by use of some form of corrugated steel filled or covered with concrete, cinder concrete being the best fireproof material. Walls are made by using terracotta or expanded metal covered with cement mortar.

Terracotta tiling is made from clay mixed with water, the plastic mass being pressed through dies to give it the requisite shape and is then baked in high temperature kilns.

The hollow blocks are formed with webs inside to give extra strength and to preserve the proper shape while drying. It cannot be safely made with walls over 1½ in. thick. Greater strength can be secured by filling the hollow spaces with concrete or brick work.

The lightness of terracotta, its enormous resisting strength, its durability and absolute indestructibility by fire, water or frost make it particularly valuable in the construction of large edifices.

Terracotta is used for floor arches; column and girder protection and for light hollow walls. There are three different grades made by varying the composition. Dense tiling is made from a mixture of clays including fireclay. Porous tiling is made by mixing sawdust with the clay which is burned out in the kiln leaving the porous clay product. Semi-porous tiling is made by mixing finely ground coal with the clay. This type of terracotta tile is a better fire resistant than either of the other types. A solid block of terracotta 1 ft. cube has borne a crushing force of over 500 tons.

Tests at Columbia University developed a crushing strength of 5,820 lb. per square inch on dense tile and 3,292 lb. per square inch on semiporous tile.

Concrete is now almost universally used for foundations, walks, basement floors and is coming into wider and wider use for pavements and for walks of building and interior supports. Concrete is an artificial stone made by cementing together sand and broken stone or similar materials by means of natural or artificial cement. Crushed stone should be about the size of hens' eggs and should be sharp and hard like granite or dike rock. Clean gravel may be used with good results for floors where not too much strength is required. Cinder concrete is cheap and satisfactory. For fireproofing this is probably the best material, but where this is used in connection with structural steel corrosive action must be guarded against, apparently due to the sulphur compounds in it.

The sand used should be clean coarse sand free from chemical salts. The best proportion of cement, sand and rock depends on the qualities of each and the purposes of the aggregate in the structure. The sand theoretically should be just the required amount to fill the voids in the aggregate, but in practice a 5 per cent excess over this amount seems advisable. Concrete will spall under the action of heat and if water is put on the heated surface the action is increased.

Hydraulic Cement.—There are three principal cements used in construction which, mixed with water and poured into the necessary forms, set and give great resistant power to crushing. The three principal hydraulic cements are: natural cement, portland cement, and puzzolan or slag cement.

Natural cement is the product resulting from calcination to a point below fusion of certain natural argillaceous limestones having approximately the correct proportions for a cementing material. The limestone is not pulverized prior to calcination, but the resulting product is ground to an impalpable powder as in the case of portland cement. The product is normally of a yellow or brownish color. Natural cement is far less uniform in quality than portland. It is considerably less strong and develops its strength (although not its set) more slowly.

Natural cements are not so uniform as to color as portland cement but vary from light to dark brown. The weight varies from 49 to 56 lb. per cubic foot and from 265 to 300 lb. per barrel. Natural cements set more quickly than portland cements,

generally within 30 min., always within an hour. Natural cement neat has a tensile strength of at least 80 lb. per square inch when 1 week old and 120 lb. per square inch at the end of 30 days, or when mixed with 1 part sand 40 lb. and 70 lb. respectively. The strength of 1 to 2 natural cement mortar is about equal to a 1 to 4 portland cement mortar.

Natural Cement Mortar and Concrete.—For stone rubble and brickwork 1 part natural cement and 3 parts sand by measure make a good mortar. For first class brickwork 1 to 2 or 1 to 1½ should be used. For concretes 1 part natural cement may be used to 2 parts sand and 4 parts gravel or crushed rock.

Kidder says "natural cement mortar possesses sufficient adhesion and crushing strength for any ordinary masonry and when mixed in the proportion of 1 to 2 is probably just as good for masonry above ground and for ordinary foundations as portland cement."

Natural cement is more suitable for works where great weight or mass rather than strength is required, such as sewers, massive foundations, dams, piers, abutments, etc., and especially for brick or stone work, either alone or mixed with lime. For this class of work it is a useful structural material which will ordinarily give satisfactory results. French natural cements branded as "Ciment Prompt" set very rapidly, often in 5 to 15 min., and their value is greatly decreased if they are disturbed after this initial set has commenced. When used therefore, the concrete should not be rammed nor tamped unless this can be done very soon after placing.

Portland Cement.—Portland cement is the product resulting from calcination to the point of incipient fusion of an intimate mixture of calcareous and argillaceous materials. The materials commonly employed are limestone, chalk, marl, etc., and clay, indurated clay, shale, etc. This cement has a definite composition varying within narrow limits. The ingredients are ground to an impalpable powder. The resulting product is normally a dull blue-gray or pearl-gray color. Portland cement is characterized by marked uniformity of quality and high strength rapidly acquired.

The chemical composition of a good portland cement will be about: Lime, 60.1 per cent; silica, 23.16; alumina, 8.5; ferric oxide, 5.3; magnesia, alkalis, sulphur trioxide, etc., 2.94 per cent. Portland cement weighs from 85 to 90 lb. per cubic foot. A barrel contains 3½ cu. ft. and weighs about 376 lb. net. When put up in sacks each weighs 94 lb. or four sacks to the barrel.

Portland cement should be used for all works which will be subject to artillery, fire, shock, abrasion, etc., for all reinforced concrete, and generally for all important works or where great strength rapidly developed is required. French portland cement is slower in hardening than American cements and precautions should be taken that the forms are not removed too soon, especially if this brings a strain on the new concrete.

Calcium sulphate delays the setting of cement. If no gypsum were added cement would be too quick setting. Amounts up to 2 per cent SO_3 are desirable but the proportion should not exceed this figure.

The influence of magnesia in cement is not as yet fully determined. Some years ago it was not thought safe to permit more than 2 per cent but now amounts up to 5 per cent are allowed. The English permit even more than do we. Magnesia comes naturally from the rock or marl used in making the cement. The methods of

chemical analysis may be found in various textbooks, but the standard specifications for testing portland cement and concrete are given on pp. 949 *et seq*.

Puzzolan or Slag Cement.—Slag cement is the product resulting from finely pulverizing a mixture of basic furnace slag (granulated by being run into water) with slaked lime without subsequent calcination. The product is light-blue to lilac in color.

Slag cement sets very slowly and never attains or maintains any great degree of hardness unless continuously wet. Accordingly it is absolutely unfitted for use above ground where it dries out and weakens. If used below ground or wherever it is continuously wet, it gives good service. It may be employed for reservoir linings or large masses of masonry submerged in water or below the ground water level. The use of slag cement is not recommended where it is practicable to obtain portland or natural cement.

A report of U. S. army engineers on "Tests in Hydraulic Cements" states that "Mortars and concretes made from puzzolan approximate in tensile strength similar mixtures of portland cement, but their resistance to crushing is considerably less. On account of its extreme fine grinding, puzzolan often gives nearly as great tensile strength in 3 : 1 mixture as neat." Slag cement weighs 330 lb. per barrel. or 82½ lb. per sack.

Concrete Mixing.—Kidder gives the following table of material required per yard (27 cu. ft.) of concrete of different mixtures.

QUANTITIES REQUIRED FOR 1 CU. YD. OF RAMMED CONCRETE. (COMPILED BY EDWIN THACHER, C. E.)

Mixtures			Stone			Gravel		
Cement	Sand	Stone	Cement, barrels	Sand, cubic yards	Stone, cubic yards	Cement, barrels	Sand, cubic yards	Gravel cubic yards
1	1.0	2.0	2.63	0.40	0.80	2.30	0.35	0.74
1	1.0	3.0	2.10	0.32	0.96	1.89	0.29	0.86
1	1.5	3.0	1.90	0.43	0.87	1.71	0.39	0.78
1	1.5	4.0	1.61	0.37	0.98	1.46	0.33	0.88
1	2.0	3.0	1.73	0.53	0.79	1.54	0.47	0.73
1	2.0	4.0	1.48	0.45	0.90	1.34	0.41	0 81
1	2.0	5.0	1.29	0.39	0.98	1.17	0.36	0.89
1	2.5	4.0	1 38	0.53	0.84	1.24	0.47	0.75
1	2.5	5.0	1.21	0.46	0.92	1.10	0.42	0.83
1	2.5	6.0	1.07	0.41	0.98	0.98	0.37	0.89
1	3.0	6.0	0.91	0.42	0.97	0.84	0.38	0.89

ACTUAL VOLUME OF RAMMED CONCRETE RESULTING FROM DIFFERENT PROPORTIONS OF INGREDIENTS. (AS DETERMINED BY MESSRS. A. W. DOW AND W. J. DOUGLAS)

Ingredients				Proportions	Quantity of concrete, cubic feet
Cement	Sand, cubic feet	Stone, cubic feet	Gravel, cubic feet		
1 bbl.	9	20¼	0	1:2:5	21.4
4½ cu. ft.	11¼	27	0	1:2½:6	27.66
or	11¼	13½	13½	1:2½:3:3	27.66
378¼ lb.	13.5		45	1:3:10	45 0

For sand and gravel mixed as it comes from the pit 125 yd. will make about 100 yd. of concrete.

Hydraulic Lime.—Hydraulic lime is the product resulting from burning a siliceous limestone. It is a natural cement containing a sufficient proportion of free lime to cause the mass to slake. The product is white to light cream in color. Hydraulic lime is not manufactured nor used in the United States, and should not be confounded with hydrated lime, a mere factory slaked quicklime, not possessing hydraulic qualities.

Hydraulic lime may be used in mortar for brick or stone work, but is unsatisfactory for concrete except in mass work, on unimportant structures where great or rapidly acquired strength is not essential. The use of hydraulic lime for any structural purposes except as a bond for brick or stone is not recommended where it is practicable to obtain portland or natural cement. Hydraulic lime is very slow setting. The time of setting may be reduced by the addition of caustic soda.

STANDARD SPECIFICATIONS FOR CEMENT, AM. SOC. FOR TEST. MAT., 1913

GENERAL CONDITIONS

1. All cement should be inspected.
2. Cement may be inspected either at the place of manufacture or on the work.
3. In order to allow ample time for inspecting and testing, the cement should be stored in a suitable weather-tight building having the floor properly blocked or raised from the ground.
4. The cement should be stored in such a manner as to permit easy access for proper inspection and identification of each shipment.
5. Every facility should be provided by the Contractor and a period of at least 12 days allowed for the inspection and necessary tests.
6. Cement should be delivered in suitable packages with the brand and name of manufacturer plainly marked thereon.
7. A bag of cement shall contain 94 lb. of cement net. Each barrel of portland cement shall contain 4 bags, and each barrel of natural cement shall contain 3 bags of the above net weight.
8. Cement failing to meet the seven-day requirements may be held awaiting the results of the 28-day tests before rejection.
9. All tests should be made in accordance with the methods proposed by the Committee on Uniform Tests of Cement of the American Society of Civil Engineers, pre-

sented to the Society January 21, 1903, and amended January 20, 1904, and January 15, 1908, with all subsequent amendments thereto. (See p. 951.)

10. The acceptance or rejection should be based on the following requirements:

NATURAL CEMENT

11. Definition. This term shall be applied to the finely pulverized product resulting from the calcination of an argillaceous limestone at a temperature only sufficient to drive off the carbonic acid gas.

Fineness

12. It shall leave by weight a residue of not more than 10 per cent on the No. 100, and 30 per cent on the No. 200 sieve.

Time of Setting

13. It shall not develop initial set in less than 10 min. and shall not develop hard set in less than 30 min. or in more than 3 hr.

Tensile Strength

14. The minimum requirements for tensile strength for briquettes 1 sq. in. in cross section shall be as follows, and the cement shall show no retrogression in strength within the periods specified:

NEAT CEMENT

AGE	STRENGTH, POUNDS
24 hours in moist air	75
7 days (1 day in moist air, 6 days in water)	150
28 days (1 day in moist air, 27 days in water)	250
ONE PART CEMENT, THREE PARTS STANDARD OTTAWA SAND	
7 days (1 day in moist air, 6 days in water)	50
28 days (1 day in moist air, 27 days in water)	125

Constancy of Volume

15. Pats of neat cement about 3 in. in diameter, ½ in. thick at center, tapering to a thin edge, shall be kept in moist air for a period of 24 hr.

(*a*) A pat is then kept in air at normal temperature.

(*b*) Another is kept in water maintained as near 70°F. as practicable.

16. These pats are observed at intervals for at least 28 days, and, to satisfactorily pass the tests, shall remain firm and hard and show no signs of distortion, checking, cracking, or disintegrating

PORTLAND CEMENT

17. Definition. This term is applied to the finely pulverized product resulting from the calcination to incipient fusion of an intimate mixture of properly proportioned argillaceous and calcareous materials, and to which no addition greater than 3 per cent has been made subsequent to calcination.

Specific Gravity

18. The specific gravity of cement shall not be less than 3.10 (3.07 for white portland). Should the test of cement as received fall below this requirement, a second test may be made upon a sample ignited at a low red heat. The loss in weight of the ignited cement shall not exceed 4 per cent.

Fineness

19. It shall leave by weight a residue of not more than 8 per cent on the No. 100, and not more than 22 per cent on the No. 200 sieve.

Time of Setting

20. It shall not develop initial set in less than 30 min., and must develop hard set in not less than 1 hr., nor more than 10 hr.

Tensile Strength

21. The minimum requirements for tensile strength for briquettes 1 sq. in. in cross section shall be asfoll ows, and the cement shall show no retrogression in strength within the periods specified:

NEAT CEMENT

AGE	STRENGTH POUNDS
24 hr. in moist air	175
7 days (1 day in moist air, 6 days in water)	500
28 days (1 day in moist air, 27 days in water)	600
ONE PART CEMENT, THREE PARTS STANDARD OTTAWA SAND	
7 days (1 day in moist air, 6 days in water)	200
28 days (1 day in moist air, 27 days in water)	300

Constancy of Volume

22. Pats of neat cement about 3 in. in diameter, ½ in. thick at the center, and tapering to a thin edge, shall be kept in moist air for a period of 24 hr.

(*a*) A pat is then kept in air at normal temperature and observed at intervals for at least 28 days.

(*b*) Another pat is kept in water maintained as near 70°F. as practicable, and observed at intervals for at least 28 days.

(*c*) A third pat is exposed in any convenient way in an atmosphere of steam, above boiling water, in a loosely closed vessel for 5 hr.

23. These pats, to satisfactorily pass the requirements, shall remain firm and hard, and show no signs of distortion, checking, cracking, or disintegrating.

SULPHURIC ACID AND MAGNESIA

24. The cement shall not contain more than 1.75 per cent of anhydrous sulphuric acid (SO_3), nor more than 4 per cent of magnesia (MgO).

REFRACTORY BRICK

Magnesia Brick are made from ground magnesite carefully selected and dead burned. It contains little silica and lime and has just the proper fluxing qualities to set at high temperatures. Magnesia bricks are used in basic openhearth steel furnaces, mechanical puddling furnaces, basic copper converters and to some extent in copper reverberatory furnaces, bullion furnaces, electric smelting, welding furnaces, calcium carbide furnaces, kilns, rotary cement kilns, etc.

Magnesia brick should be laid in magnesite cement made of ground magnesite and 20 to 25 per cent fireclay. They are good conductors of heat and should be backed up with other material if used where this heat conductivity would injure plate or frame work. They expand sufficiently on heating so that when laid as the lining of circular converters, etc., every four or five courses should have a slip of lath laid in which on burning out allows the brick to expand without deforming the arch.

They are better conductors of electricity than porcelain at 2,000°F. or over; at low temperatures this conductivity is less than porcelain. The best results are obtained from magnesia brick in furnaces where continuous heats are used. Great variations of temperature, exposure while hot to currents of cold air or to contact while hot with water or oil will cause them to shatter and spall. They should not be subjected to excessive weight when hot.

Chrome brick are made from chrome ore ($FeCrO_2$) which is exceedingly refractory, dense and neutral. It is neither acid, basic, reducing, nor oxidizing and is practically infusible.

Chrome brick are used in basic openhearth steel furnaces between firebrick and magnesia brick courses on the bottom, for lining ports, uptakes, etc., along the slag line in steel-heating furnaces, copper-smelting and refining furnaces, lining settlers, converters next to the shell, lead softening and refining furnaces, cement kilns, etc.[1]

Chrome brick should be laid in finely ground chrome ore except when they are laid next a steel plate shell when they should be laid in magnesite cement which sticks well to iron work. Chrome bricks are useful in making quick repairs in furnaces at working heat as they are not affected by sudden changes of temperature. At furnace heat they can come in contact with water without breaking or spalling, but they should not be subjected to excessive pressure when hot.

Ganister and dinas brick are English brick made from rock containing about 82 per cent and 98 per cent respectively of silica. They are no longer much used in this country since the development of high-grade brick manufacture here. Glazed or vitrified brick will neither absorb nor give off heat as rapidly as porous or non-vitrified material.

Firebrick are made by combining certain proportions of hard or flint clays and of soft or plastic clays. The former are the heat resisting elements of the mass. The latter softens at a lower temperature and act as a bond binding the hard-clay fragments together when the brick is burned giving a homogeneous mass of requisite physical strength.

This fireclay is a combination of silica and alumina essentially always in combination with greater or less quantities of impurities such as lime, iron, magnesia,

[1] However, it should be noted that both magnesite and chrome brick have one great objection when used in non-ferrous metallurgy. If used in contact with the metal they absorb some of it and it is then difficult to recover. Particularly is this true with chrome bricks, which are impossible to smelt.—EDITOR.

alkalis and titanic acid. The quality of the firebrick depends on the proportions of the silica and alumina.

A good firebrick must give the maximum of resistance to either heat or abrasion with the minimum of contraction or expansion.

For laying firebrick a fireclay of the same quality as the brick should be used, using as little of it as possible, by laying a tight brick to brick joint.

The joints in brickwork are the weakest points and if laid with inferior clay it will melt and run before the bricks are affected leaving open points where the flame and slag easily attack the lining. A low-grade clay will often melt and flux the higher grade firebrick destroying the arch or walls which they compose.

Tables giving the number of brick required in circles or arches of any diameter laid up with straight, wedge and key bricks are given in various handbooks and catalogs of the manufacturers.

Firebrick for boiler settings must fulfill different requirements. "In some cases the best brick to use depends entirely upon the heat-resisting quality; in others, upon resistance to the impinging action of flame and spalling; while in others, upon the ability to resist the action of clinker and poker, together with heat-resisting qualities." (Harbison-Walker.)

Silica brick are made of sand or calcined flints (almost pure silica). Containing no clay this material does not become plastic when wet, therefore, it has to be mixed with some material to bind the silica particles together. About 1 per cent of lime is used which forms a small quantity of silicate of lime and acts as a binder. Silica brick are very fragile and have a slight but uniform known expansion and are better conductors of heat than fireclay brick, but they are very refractory. They are the most widely used brick for copper smelting furnaces, reverberatories, etc., but because of their high heat conductivity have to be backed with firebrick. They are used in byproduct oven construction, as they decrease the time required for coking by reason of this greater conductivity.

Special shapes are made for roof arches, door jambs, skewbacks, etc. On account of the severity of the service they are also used for lining the flues leading from smelting furnaces to waste heat boilers, etc. However, they are acid and will slag in furnaces in the presence of molten basic charges unless proper amounts of extraneous silica or highly siliceous ores are added to the molten bath. The side walls of reverberatory furnaces are protected by charging this siliceous material through side ports or through holes in its roof arch. This is known as fettling.

For the best results silica brick should be laid in silica cement, composed of silica sand and about 20 to 25 per cent fine clay. The quantity required to lay 1,000 bricks is about 1,500 lb. or 1,000 lb. if they are dipped.

Sudden variations of temperature cause silica brick to spall and reduce their refractoriness. Furnaces in which they are used should be heated or cooled gradually.

Weight of brickwork per cubic foot runs about as follows: Common red brick, 100 lb.; fireclay, 150 lb.; silica, 128 lb.; chrome, 175 lb.; magnesia, 160 lb.

The Harbison-Walker Refractories Co. gives the following general rules regarding brickwork. All firebrick should be kept in a dry place. Moisture especially in cold weather will greatly injure any firebrick.

To obtain the best results from brickwork, observe the following precautions: Use good fireclay to lay. The fireclay should be equal in refractoriness to the brick itself, mixing with water to a thin soup. Dip brick and rub to make a brick-to-brick joint. From 250 to 350 lb. of fireclay are sufficient to lay 1,000 brick.

Heat slowly to expel moisture as it is absolutely essential to dry out brickwork thoroughly. Firing the boiler while the brickwork is green will always result in opening up cracks in the setting. If possible, as soon as stack connections are made, damper and ashpit doors should be blocked open to allow circul tion of air.

After filling the boiler with water a light fire of shavings should be kindled, gradually increasing the wood fire, and if possible, continuing several days until the walls are thoroughly dried out.

For estimating on firebrick work, use the following figures:

1 sq. ft. of 4½-in. wall requires 7 brick;
1 sq. ft of 9-in. wall requires 14 brick;
1 sq. ft. of 13½-in. wall requires 21 brick;
1 cu. ft. of brickwork requires 17 nine-inch straight brick;
1 cu. ft. of fireclay brickwork weighs 150 lb.;
1 cu. ft. of silica brickwork weighs 130 lb.;
1,000 brick (closely stacked) occupy 56 cu. ft.;
1,000 brick (loosely stacked) occupy 72 cu. ft.

For estimating on red brickwork, figure on 9 cu. ft. of sand and 3 bu. of lime for laying 1,000 brick.

Common Brick.—Common brick formerly were made from clay pressed into molds by hand or machinery and baked in kilns. At present bricks made from sand and lime are extensively used, while they have been used in Europe for 50 years.

According to their position in the kiln, common brick are designated as *arch* or hard burned brick, *red* or well burned brick, and salmon or soft brick. As a rule, salmon brick are not fit for use in an exterior or bearing wall.

The color of brick depends on the presence of iron, lime, and magnesia in the clay; iron giving them the characteristic red color when burned. There is no legal standard size for common brick. In the Eastern states they average 7¾ by 3¾ by 2¼ in., and in the Western states 8½ by 4⅛ by 2½ in. The weight varies from 4½ to 5½ lb. each.

Common brick are ordinarily laid in lime mortar made of 1 part lime paste and 2 parts sand, this having been determined from experiments by Government engineers to be the best proportion. Lime for this purpose is produced by the calcining limestone or shells in kilns and is a soft white substance which slakes rapidly in open air. It is usually sold in barrels weighing 220 lb. each or is sold by the bushel of 80 lb.; 2½ bu. or 200 lb. being considered equivalent to a barrel. Lime paste yields about 2.62 times the bulk of unslaked lime. A barrel of average lime makes about 8 cu. ft. or 20 buckets of lime paste. Cement mortar is also used.

To lay 1,000 common brick about 2½ bu. or 1 bbl. of lime and ⅝ yd. of sand are required: For lime cement mortar 2 bu. lime, 1 bbl. cement and ⅝ yd. of sand: For 1:3 cement mortar, 1½ bbl. cement and ⅝ yd. of sand are required. Sand from pits or banks free from clay and earthy material are considered best for mortar although some river bed sand is used. Sea sand contains alkaline salts which cause efflorescence when used in brickwork.

The use of sand in mortar is to prevent excessive shrinkage and save lime and when used in the proportion 1:2 strengthens it. Sand added to cement gives a weaker mixture than neat cement.

Kidder gives the following safe-working loads for masonry in walls or piers:

	Tons per square feet Eastern brick	Western brick
Red brick in lime mortar	7	5
Red brick in natural cement mortar 1:3	10	8
Arch brick in lime mortar	8	6
Arch brick in natural cement	12	9
Arch brick in Portland cement	15	12½

Plain wall are generally figured at 15 bricks per square foot of 8 or 9 in. wall; 22½ bricks per square foot 12 or 13 in. wall, 30 bricks per square foot of 16 or 17 in. wall and 7½ bricks for each additional 4 or 4½ in. in thickness of the wall.

CONCRETE MAKING MATERIALS AND CEMENT TESTING

By S. S. Sadtler[1]

The quality of the cement to be used is determined by chemical analysis together with physical tests. Probably the most important test of all is the soundness or boiling test. The presence of much free lime not well distributed by initial grinding and sintering tends to cause unsoundness in use with consequent cracking and expansion. Much trouble may be saved by refusing shipments that do not meet specifications in this particular (see p. 958).

Sand.—As all kinds of local sand must be used in making concrete one cannot be iron clad as to general specifications. Sand should always be levigated. Seashore sand is naturally free from clay. So are river sands, but bank sands must be washed to render them suitable. This is best done by the producer who handles the sand by conveyors whereas the user would probably have to depend upon hand shoveling into the washing trough which costs more and the sand is not apt to be so well washed. The product will be wet and allowance will have to be made for the difference in volume of wet and dry sand. Sand shoveled but not packed contains about 45 per cent voids, while sand saturated with water has about 38 per cent. Of course, the presence of water in the voids of the sand is considered as being the same as air. The great desideratum in concrete is to have the maximum density (free from air when set). Sand and aggregates are used jointly so as to secure without sacrifice of strength the greatest amount of natural unmanufactured material suitable to the concrete. It has been found that the use of both sand and aggregate gives the best net result. As to the sand itself it might naturally be supposed that the greatest latitude in sizes would produce the best result. This is not altogether the case, the best mixture being fine and coarse, with no sand of intermediate fineness. The finer sand must be small enough to fit into the voids of the coarse. The coarse sand should pass a 4-mesh and be held by a 20-mesh sieve. The fine sand should pass a 40-mesh, and of course contain no appreciable amount of clay.

The voids in fine sand (if the grains were perfect spheres) are in just the same proportion as if the sand were all coarse, but manifestly fine particles can fill into the

[1] Chemical engineer, S. P. Sadtler & Son, Philadelphia, Pa.

voids of the coarse, and what we are aiming to accomplish is this: Fill the voids of aggregate with coarse sand, the voids of the coarse sand with fine sand and the voids of the fine sand with Portland cement. This grading of the sand necessitates discarding a portion of the sand after screening and using the discard for other purposes. In practice sand is only screened for securing the best results obtainable. For ground floors it is not necessary to have a concrete as rich in cement as is required for arches, pillars, etc. A mixture 1:4:8 is sufficient if properly tamped or rolled. If rolled, very light rollers are used. The thickness of this concrete is generally from 3 to 5 in. depending upon the character of the bottom.

When cinders are used more cement is required and somewhat less sand. Instead of 1:4:8 it would probably be 1:3:6. This is due to the fines in the cinders and the relatively large amount of surface to be covered by the cement and sand. Cinders from power plants using soft coal only should be used and they should be screened. All that passed a ⅜-in. screen should be discarded.

Surfacing.—For the final coat for floors, etc. a mixture of cement and sand only is used and this is quite rich, 1:2 being used. This is well troweled so as to bring the cement to the surface. It is almost superfluous to say that concrete that is not tamped must be free flowing. For surface work it is used not quite so wet, as the trowelling is an aid in removing voids, but it must flow easily with the aid of trowelling.

After floors have had several weeks setting and begin to dry out, wherever there is much walking or any trucking whatever it pays to paint the surface with oil. Raw linseed oil is used and to secure greater penetration add 1 per cent each of turpentine and denatured alcohol. This treatment adds to the first cost but it pays in the end. It need not be done all over the floor of the average works, where machinery is permanently installed, but only in the aisles and in front of machines and wherever else the cement would be abraded. One cubic yard of 1:2 cement mortar contains about 3 bbl. or 12 bags of cement.

Aggregates.—Broken stone and screened gravel are the best materials for this purpose and may be used in the proportions given above, say 1:2:4 for arches and 1:3:6 for piers. When the mixture with the cements and sand is made in power mixers it is always more uniform and takes less cement for the same strength of structure. Cinders are rarely used except for floors.

Small cement tanks, pipes, etc., are made of 1:3 to 1:4 mortar and tamped. The sand is carefully selected and for nice work is graded, taking only medium coarse and fine sand. A good formula is 20 to 40 and through 80 for small work and 10 to 20 and through 40 for larger. Waterproofing substances such as sold by the cement companies (composed of soap mixtures) or about 1 per cent of medium heavy lubricating oil on the weight of cement may be used, but careful proportioning of sand and cement, careful grading of the sand, tamping or the use of a cement gun generally renders other waterproofing unnecessary. Great care must be taken to keep work wet for 2 weeks after the preliminary set.

For making very small tanks it is desirable to use white portland cement and white plasterer's sand so as to secure a nice looking article.

Steel articles do not rust when well embedded in cement or concrete. Steel rods are used for reinforcing nearly all concrete work where the maximum strength with the minimum cement is aimed at. For small objects, chicken wire (large or small mesh) or even finer screening is used.

Cement and concrete are used for holding neutral and slightly alkaline liquids. For cases where mild acid mixtures come in contact with it, such as in superphosphate, dense siliceous aggregates must be used with heavy walls and with moderately lean

cement mixtures that are well tamped. The writer would think 10 to 20 per cent of ground silica could be used to advantage in the cement but as this would affect its strength adversely the mixture could not be made so lean as in the case just mentioned.

Where concrete is laid in winter it is generally sufficiently covered with forms to protect it in most climates. In the case of floors, marsh hay, etc., is covered over after laying. In anything approaching zero weather salt may be added to quite a large extent. The writer has been told by a competent engineer who has built much in cold weather that he used freely 10 per cent of salt to the cement taken, in the water, without seriously affecting the strength of the work.

Acidproofing.—After the surface coating has been put on concrete for floors they can be made more or less resistant to acids in various ways. Washing with a 20 per cent aqueous aluminum sulphate solution and, when dry, painting with linseed oil is referred to on page 950. For making cisterns to hold acid the concrete should be painted with acidproof bituminous composition and then lined with acidproof brick laid in hot asphalt mastic.

Rosendale cement is lower in lime than portland and does not develop more than half the strength of the latter so can not be used with as much sand and aggregate. It is less basic and may have some application where acids would come in contact with the work, it is practically off the market, however, in this country.

A quick and very good test as to the chemical suitability of sand or gravel for concrete construction is to shake with a 3 per cent solution of sodium hydroxide, about 150 c.c. of solution to 100 g. of sand, allow the mixture to stand over night and note the color of the supernatant solution. A suitable sand will give a colorless or very light-brown solution. One containing much humus will give a dark solution and should be rejected.

The percentage of voids may be quickly tested by taking 100 g. of dry sand and pouring it into a dry 100 c.c. graduate, shaking or tapping until the sand is compacted and note the volume, V, occupied. Put 50 c.c. of water in another 100 c.c. graduate and pour the sand slowly into the water. (It is more difficult to avoid entrapped air if the water is poured into the sand, although it can be slowly flowed down the side of the graduate and the air slowly displaced from the sand.) Note the volume, v, of the combined water and sand. Then:

$$\text{percentage of voids} = \frac{50 - (v - V)}{V}$$

Portland Cement Testing.—The best tests for portland cement are those given by the American Society for Testing Materials, and are as follows:

1. Portland cement is the product obtained by finely pulverizing clinker produced by calcining to incipient fusion, an intimate and properly proportioned mixture of argillaceous and calcareous materials, with no additions subsequent to calcination excepting water and calcined or uncalcined gypsum.

I. Chemical Properties

2. The following limits shall not be exceeded:

Loss on ignition, per cent	4.00
Insoluble residue, per cent	0.85
Sulphuric anhydride (SO_3), per cent	2.00
Magnesia (MgO), per cent	5.00

II. Physical Properties

3. The specific gravity of cement shall be not less than 3.10 (3.07 for white portland cement). Should the test of cement as received fall below this requirement a second test may be made upon an ignited sample. The specific gravity test will not be made unless specifically ordered.

4. The residue on a standard No. 200 sieve shall not exceed 22 per cent by weight.

5. A pat of neat cement shall remain firm and hard, and show no signs of distortion, cracking, checking, or disintegration in the steam test for soundness.

6. The cement shall not develop initial set in less than 45 min. when the Vicat needle is used or 60 min. when the Gilmore needle is used. Final set shall be attained within 10 hr.

7. The average tensile strength in pounds per square inch of not less than three standard mortar briquettes (see p. 957) composed of 1 part cement and 3 parts standard sand, by weight, shall be equal to or higher than the following:

Age of test, days	Storage of briquettes	Tensile strength, pounds per square inch
7	1 day in moist air, 6 days in water	200
28	1 day in moist air, 27 days in water	300

8. The average tensile strength of standard mortar at 28 days shall be higher than the strength at 7 days.

III. Packages; Marking and Storage

9. The cement shall be delivered in suitable bags or barrels with the brand and name of the manufacturer plainly marked thereon, unless shipped in bulk. A bag shall contain 94 lb. net. A barrel shall contain 376 lb. net.

10. The cement shall be stored in such a manner as to permit easy access for proper inspection and identification of each shipment, and in a suitable weather-tight building which will protect the cement from dampness.

IV. Inspection

11. Every facility shall be provided the purchaser for careful sampling and inspection at either the mill or at the site of the work, as may be specified by the purchaser. At least 10 days from the time of sampling shall be allowed for the completion of the 7-day test, and at least 31 days shall be allowed for the completion of the 28-day test. The cement shall be tested in accordance with the methods hereinafter prescribed. The 28-day test shall be waived only when specifically so ordered.

V. Rejection

12. The cement may be rejected if it fails to meet any of the requirements of these specifications.

13. Cement shall not be rejected on account of failure to meet the fineness requirement if upon retest after drying at 100°C. for 1 hr. it meets this requirement.

14. Cement failing to meet the test for soundness in steam may be accepted if it passes a retest using a new sample at any time within 28 days thereafter.

15. Packages varying more than 5 per cent from the specified weight may be rejected; and if the average weight of packages in any shipment, as shown by weighing 50 packages taken at random, is less than that specified, the entire shipment may be rejected.

TESTS

VI. Sampling

16. Tests may be made on individual or composite samples as may be ordered. Each test sample should weigh at least 8 lb.

17. (*a*) *Individual Sample.*—If sampled in cars one test sample shall be taken from each 50 bbl. or fraction thereof. If sampled in bins one sample shall be taken from each 100 bbl.

(*b*) *Composite Sample.*—If sampled in cars one sample shall be taken from one sack in each 40 sacks (or 1 bbl. in each 10 bbl.) and combined to form one test sample. If sampled in bins or warehouses one test sample shall represent not more than 200 bbl.

18. Cement may be sampled at the mill by any of the following methods that may be practicable, as ordered:

(*a*) *From the Conveyor Delivering to the Bin.*—At least 8 lb. of cement shall be taken from approximately each 100 bbl. passing from the conveyor.

(*b*) *From Filled Bins by Means of Proper Sampling Tubes.*—Tubes inserted vertically may be used for sampling cement to a maximum depth of 10 ft. Tubes inserted horizontally may be used where the construction of the bin permits. Samples shall be taken from points well distributed over the face of the bin.

(*c*) *From Filled Bins at Points of Discharge.*—Sufficient cement shall be drawn from the discharge openings to obtain samples representative of the cement contained in the bin, as determined by the appearance at the discharge openings of indicators placed on the surface of the cement directly above these openings before drawing of the cement is started.

19. Samples preferably shall be shipped and stored in airtight containers. Samples shall be passed through a sieve having 20 meshes per linear inch in order to mix the sample thoroughly, break up the lumps and remove foreign materials.

VII. Chemical Analysis

Loss on Ignition

20. One gram of cement shall be heated in a weighed covered platinum crucible, of 20 to 25-c.c. capacity, as follows, using either method (*a*) or (*b*) as ordered:

(*a*) The crucible shall be placed in a hole in an asbestos board, clamped horizontally so that about three-fifths of the crucible projects below, and blasted at a full red heat for 15 min. with an inclined flame; the loss in weight shall be checked by a second blasting for 5 min. Care shall be taken to wipe off particles of asbestos that may adhere to the crucible when withdrawn from the hole in the board. Greater neatness and shortening of the time of heating are secured by making a hole to fit the crucible in a circular disc of sheet platinum and placing this disc over a somewhat larger hole in an asbestos board.

(*b*) The crucible shall be placed in a muffle at any temperature between 900 and 1,000°C. for 15 min. and the loss in weight shall be checked by a second heating for 5 min.

21. A permissible variation of 0.25 will be allowed, and all results in excess of the specified limit but within this permissible variation shall be reported as 4 per cent.

Insoluble Residue

22. To a 1-g. sample of cement shall be added 10 c.c. of water and 5 c.c. of concentrated hydrochloric acid; the liquid shall be warmed until effervescence ceases. The solution shall be diluted to 50 c.c. and digested on a steam bath or hot plate until it is evident that decomposition of the cement is complete. The residue shall be filtered, washed with cold water, and the filter paper and contents digested in about 30 c.c. of a 5 per cent solution of sodium carbonate, the liquid being held at a temperature just short of boiling for 15 min. The remaining residue shall be filtered, washed with cold water, then with a few drops of hot hydrochloric acid, 1:9, and finally with hot water, and then ignited at a red heat and weighed as the insoluble residue.

23. A permissible variation of 0.15 will be allowed, and all results in excess of the specified limit but within the permissible limit shall be reported as 0.85 per cent.

Sulphuric Anhydride

24. One gram of the cement shall be dissolved in 5 c.c. of concentrated hydrochloric acid diluted with 5 c.c. of water, with gentle warming; when solution is complete 40 c.c. of water shall be added, the solution filtered, and the residue washed thoroughly with water. The solution shall be diluted to 250 c.c., heated to boiling and 10 c.c. of a hot 10 per cent solution of barium chloride shall be added slowly, drop by drop, from a pipette and the boiling continued until the precipitate is well formed. The solution shall be digested on the steam bath until the precipitate has settled. The precipitate shall be filtered, washed, and the paper and contents placed in a weighed platinum crucible and the paper slowly charred and consumed without flaming. The barium sulphate shall then be ignited and weighed. The weight obtained multiplied by 34.4 gives the percentage of sulphuric anhydride. The acid filtrate obtained in the determination of the insoluble residue may be used for the estimation of sulphuric anhydride instead of using a separate sample.

25. A permissible variation of 0.10 will be allowed, and all results in excess of the specified limit but within this permissible variation shall be reported as 2.00 per cent.

Magnesia

26. To 0.5 g. of the cement in an evaporating dish shall be added 10 c.c. of water to prevent lumping and then 10 c.c. of concentrated hydrochloric acid. The liquid shall be gently heated and agitated until attack is complete. The solution shall then be evaporated to complete dryness on a steam or water bath. To hasten dehydration the residue may be heated to 150 or even 200°C. for ½ to 1 hr. The residue shall be treated with 10 c.c. of concentrated hydrochloric acid diluted with an equal amount of water. The dish shall be covered and the solution digested for 10 min. on a steam bath or water bath. The diluted solution shall be filtered and the separated silica washed thoroughly with water.[1] Five cubic centimeters of concentrated hydrochloric acid and sufficient bromine water to precipitate any manganese which may be present, shall be added to the filtrate (about 250 c.c.). This shall be made alkaline with ammonium hydroxide, boiled until there is but a faint odor of ammonia,

[1] Since this procedure does not involve the determination of silica, a second evaporation is unnecessary.

and the precipitated iron and aluminum hydroxides, after settling, shall be washed with hot water, once by decantation and slightly on the filter. Setting aside the filtrate, the precipitate shall be transferred by a jet of hot water to the precipitating vessel and dissolved in 10 c.c. of hot hydrochloric acid. The paper shall be extracted with acid, the solution and washings being added to the main solution. The aluminum and iron shall then be reprecipitated at boiling heat by ammonium hydroxide and bromine water in a volume of about 10 c.c., and the second precipitate shall be collected and washed on the filter used in the first instance if this is still intact. To the combined filtrates from the hydroxides of iron and aluminum, reduced in volume if need be, 1 c.c. of ammonium hydroxide shall be added, the solution brought to boiling, 25 c.c. of a saturated solution of boiling ammonium oxalate added, and the boiling continued until the precipitated calcium oxalate has assumed a well-defined granular form. The precipitate after 1 hr. shall be filtered and washed, then with the filter shall be placed wet in a platinum crucible, and the paper burned off over a small flame of a bunsen burner; after ignition it shall be redissolved in hydrochloric acid and the solution diluted to 100 c.c. Ammonia shall be added in slight excess, and the liquid boiled. The lime shall then be reprecipitated by ammonium oxalate, allowed to stand until settled, filtered and washed. The combined filtrates from the calcium precipitates shall be acidified with hydrochloric acid, concentrated on the steam bath to about 150 c.c., and made slightly alkaline with ammonium hydroxide, boiled and filtered (to remove a little aluminum and iron and perhaps calcium). When cool, 10 c.c. of saturated solution of sodium-ammonium-hydrogen phosphate shall be added with constant stirring.[1] When the crystalline ammonium-magnesium orthophosphate has formed, ammonia shall be added in moderate excess. The solution shall be set aside for several hours in a cool place, filtered and washed with water containing 2.5 per cent of NH_3. The precipitate shall be dissolved in a small quantity of hot hydrochloric acid, the solution diluted to about 100 c.c., 1 c.c. of a saturated solution of sodium-ammonium-hydrogen phosphate added, and ammonia drop by drop, with constant stirring, until the precipitate is again formed as described and the ammonia is in moderate excess. The precipitate shall then be allowed to stand about 2 hr., filtered and washed as before. The paper and contents shall be placed in a weighed platinum crucible, the paper slowly charred, and the resulting carbon carefully burned off. The precipitate shall then be ignited to constant weight over a Meker burner, or a blast not strong enough to soften or melt the pyrophosphate. The weight of magnesium pyrophosphate obtained multiplied by 72.5 gives the percentage of magnesia. The precipitate so obtained always contains some calcium and usually small quantities of iron, aluminum, and manganese as phosphates.[2]

27. A permissible variation of 0.4 will be allowed, and all results in excess of the specified limit but within this permissable variation shall be reported as 5.00 per cent.

VIII. Determination of Specific Gravity

28. The determination of specific gravity shall be made with a standardized Le Chatelier apparatus. This apparatus is standardized by the United States Bureau of Standards. Kerosene free from water, or benzine not lighter than 62°Bé, shall be used in making this determination.

[1] In this stirring the sides of the beaker should be hit by the stirring rod as little as possible, for where the beaker is touched the precipitate sticks tenaciously. Some authorities say complete precipitation is not obtaining except by "scratching the beaker." Undoubtedly higher results can be obtained by scratching off some of the beaker into the precipitate, but the result is not ammonium-magnesium phosphate.—EDITOR.

[2] If the last washing is given with a 10 per cent solution of ammonium nitrate containing 2.5 per cent of free ammonia it is much easier to burn the precipitate white. Indeed it can usually be done without blasting. The use of an asbestos mat on a tared Gooch crucible is infinitely preferable to filter paper for filtering magnesias.—EDITOR.

29. The flask shall be filled with either of these liquids to a point on the stem between zero and 1 c.c., and 64 g. of cement, of the same temperature of the liquid, shall be slowly introduced, taking care that the cement does not adhere to the inside of the flask above the liquid and to free the cement from air by rolling the flask in an inclined position. After all the cement is introduced, the level of the liquid will rise to some division of the graduated neck; the difference between readings is the volume displaced by 64 g. of the cement.

The specific gravity shall be obtained from the formula

$$\text{Specific gravity} = \frac{\text{weight of cement grams}}{\text{displaced volume cubic centimeters}}$$

30. The flask, during the operation, shall be kept immersed in water, in order to avoid variations in the temperature of the liquid in the flask, which shall not exceed 0.5°C. The results of repeated tests shall agree within 0.01.

31. The determination of specific gravity shall be made on the cement as received; if it falls below 3.10, a second determination shall be made after igniting the sample as described in Section 20.

IX. Determination of Fineness

32. Wire cloth for standard sieves for cement shall be woven (not twilled) from brass, bronze, or other suitable wire, and mounted without distortion on frames not less than 1½ in., below the top of the frame. The sieve frames shall be circular, approximately 8 in. in diameter, and may be provided with a pan and cover.

33. A standard No. 200 sieve is one having nominally an 0.0029-in. opening and 200 wires per inch standardized by the U. S. Bureau of Standards, and conforming to the following requirements:

The No. 200 sieve should have 200 wires per inch, and the number of wires in any whole inch shall not be outside the limits of 192 to 208. No opening between adjacent parallel wires shall be more than 0.0050 in. in width. The diameter of the wire shall be more than 0.0050 in. in width. The diameter of the wire should be 0.0021 in. and the average diameter shall not be outside the limits of 0.0019 to 0.0023 in. The value of the sieve as determined by sieving tests made in conformity with the standard specification for these tests on a standardized cement which gives a residue of 25 to 20 per cent on the No. 200 sieve, or on other similarly graded material, shall not show a variation of more than 1.5 per cent above or below the standards maintained at the Bureau of Standards.

34. The test shall be made with 50 g. of cement. The sieve shall be thoroughly clean and dry. The cement shall be placed on the No. 200 sieve, with pan and cover attached, if desired, and shall be held in one hand in a slightly inclined position so that the sample will be well distributed over the sieve, at the same time gently striking the side about 150 times per minute against the palm of the other hand on the up stroke. The sieve shall be turned every 25 strokes about one-sixth of a revolution in the same direction. The operation shall continue until not more than 0.05 g. passes through in 1 min. of continuous sieving. The fineness shall be determined from the weight of the residue on the sieve expressed as a percentage of the weight of the original sample.

35. Mechanical sieving devices may be used, but the cement shall not be rejected if it meets the fineness requirement when tested by the hand method described in Section 34.

36. A permissible variation of 1 per cent will be allowed, and all results in excess of the specified limit but within this permissible variation shall be reported as 22 per cent.

X. Mixing Cement Pastes and Mortars

37. The quality of dry material to be mixed at one time shall not exceed 1,000 g. nor be less than 500 g. The proportions of cement or cement and sand shall be stated by weight in grams of the dry materials; the quantity of water shall be expressed in cubic centimeters (1 c.c. of water = 1 g.). The dry materials shall be weighed, placed upon a non-absorbent surface, thoroughly mixed dry if sand is used, and a crater formed in the center, into which the proper percentage of clean water shall be poured; the material on the outer edge shall be turned into the crater by the aid of a trowel. After an interval of ½ min. for the absorption of the water the operation shall be completed by continuous, vigorous mixing, squeezing and kneading with the hands for at least 1 min.[1] During the operation of mixing, the hands should be protected by rubber gloves.

38. The temperature of the room and the mixing water shall be maintained as nearly as practicable at 21°C. (70°F.).

XI. Normal Consistency

39. The Vicat apparatus consists of a frame bearing a movable rod weighing 300 g., one end being 1 cm. in diameter for a distance of 6 cm., the other having a removable needle, 1 mm. in diameter, 6 cm. long. The rod is reversible, and can be held in any desired position by a screw, and has midway between the ends a mark which moves under a scale (graduated to millimeters) attached to the frame. The paste is held in a conical, hard-rubber ring, 7 cm. in diameter at the base, 4 cm. high, resting on a glass plate about 10 cm. square.

40. In making the determination 500 g. of cement, with a measured quantity of water, shall be kneaded into a paste, as described in Section 37, and quickly formed into a ball with the hands, completing the operation by tossing it six times from one hand to the other, maintained about 6 in. apart; the ball resting in the palm of one hand shall be pressed into the larger end of the rubber ring held in the other hand, completely filling the ring with paste; the excess at the larger end shall be removed by a single movement on the palm of the hand; the ring shall then be placed on its larger end on a glass plate and excess paste at the smaller end sliced off at the top of the ring by a single oblique stroke of a trowel held at a slight angle with the top of the ring. During these operations care shall be taken not to compress the paste. The paste confined in the ring, resting on the plate, shall be placed under the rod, the larger end of which shall be brought in contact with the surface of the paste; the scale shall be then read, and the rod quickly released. The paste shall be of normal consistency when the rod settles to a point 10 mm. below the original surface in ½ min. after being released. The apparatus shall be free from all vibrations during the test. Trial pastes shall be made with varying percentages of water until the normal consistency is obtained. The amount of water required shall be expressed in percentage by weight of the dry cement.

41. The consistency of standard mortar shall depend on the amount of water required to produce a paste of normal consistency from the same sample of cement. Having determined the normal consistency of the sample, the consistency of standard mortar made from the same sample shall be as indicated in Table I, the values being in percentage of the combined dry weights of the cement and standard sand.

[1] In order to secure uniformity in the results of tests for the time of setting and tensile strength the manner of mixing above described should be carefully followed. At least 1 min. is necessary to obtain the desired plasticity which is not appreciably affected by continuing the mixing for several minutes. The exact time necessary is dependent upon the personal equation of the operator. The error in mixing should be on the side of over mixing.

TABLE I.—PERCENTAGE OF WATER FOR STANDARD MORTARS

Percentage of water for neat cement paste of normal consistency	Percentage of water for one cement, three standard Ottawa sand	Percentage of water for neat cement paste of normal consistency	Percentage of water for one cement, three standard Ottawa sand
15	9.0	23	10.3
16	9.2	24	10.5
17	9.3	25	10.7
18	9.5	26	10.8
19	9.7	27	11.0
20	9.8	28	11.2
21	10.0	29	11.3
22	10.2	30	11.5

XII. Determination of Soundness[1]

42. A steam apparatus, which can be maintained at a temperature between 98 and 100°C., is to be used. The capacity of this apparatus may be increased by using a rack for holding the pats in a vertical or inclined position.

43. A pat from cement paste of normal consistency about 3 in. in diameter, ½ in. thick at the center, and tapering to a thin edge, shall be made on clean glass plates about 4 in. square, and stored in moist air for 24 hr. In molding the pat, the cement paste shall be first flattened on the glass and the pat then formed by drawing the trowel from the outer edge toward the center.

44. The pat shall then be placed in an atmosphere of steam at a temperature between 98 and 100°C. upon a suitable support 1 in. above boiling water for 5 hr.

45. Should the pat leave the plate, distortion may be detected best with a straight edge applied to the surface which was in contact with the plate.

XIII. Determination of Time of Setting

46. The following are alternate methods, either of which may be used as ordered:

47. The time of setting shall be determined with the Vicat apparatus described in section 39.

48. A paste of normal consistency shall be molded in the hard-rubber ring as described in Section 40, and placed under the rod, the smaller end of which shall then be carefully brought in contact with the surface of the paste, and the rod quickly released. The initial set shall be said to have occurred when the needle ceases to pass a point 5 mm. above the glass plate in ½ min. after being released; and the final set, when the needle does not sink visibly into the paste. The test pieces shall be kept in moist air during the test. This may be accomplished by placing them on a rack over water contained in a pan and covered by a damp cloth, kept from contact with them by means of a wire screen; or they may be stored in a moist closet. Care shall be taken to keep the needle clean as the collection of cement on the sides of the needle retards the penetration, while cement on the point may increase the penetra-

[1] Unsoundness is usually manifested by change in volume which causes distortion, cracking, checking or disintegration.

Pats improperly made or exposed to drying may develop what are known as shrink-cracks within the first 24 hrs. and are not an indication of unsoundness.

The failure of the pats to remain on the glass or the cracking of the glass to which the pats are attached does not necessarily indicate unsoundness.

tion. The time of setting is affected not only by the percentage and temperature of the water used and the amount of kneading the paste received, but by the temperature and humidity of the air, and its determination is therefore only approximate.

49. The time of setting shall be determined by the Gilmore needles.

50. The time of setting shall be determined as follows: A pat of neat cement paste about 3 in. in diameter and ½ in. in thickness with a flat top, mixed to a normal consistency, shall be kept in moist air at a temperature maintained as nearly as practicable at 21°C. (70°F.). The cement shall be considered to have acquired its initial set when the pat will bear, without appreciable indentation, the Gilmore needle $\frac{1}{12}$ in. in diameter, loaded to weigh ¼ lb. The final set has been acquired when the pat will bear without appreciable indentation, the Gilmore needle $\frac{1}{24}$ in. in diameter, loaded to weigh 1 lb. In making the test, the needles shall be held in a vertical position, and applied lightly to the surface of the pat.

XIV. Extension Tests

51. The usual form of test piece shall be used. The molds shall be made of noncorroding metal and have sufficient material in the sides to prevent spreading during molding. Molds shall be wiped with an oily cloth before using.

52. The sand to be used shall be natural sand from Ottawa, Ill., screened to pass a No. 20 sieve and retained on a No. 30 sieve. This sand may be obtained from the Ottawa Silica Co., at a cost of 2 cts. per pound, f.o.b. cars, Ottawa, Ill.

53. This sand, having passed the No. 20 sieve, shall be considered standard when not more than 5 g. pass the No. 30 sieve after 1 min. continuous sieving of a 500-g. sample.

54. The sieves shall conform to the following specifications:

The No. 20 sieve shall have between 19.5 and 20.5 wires per whole inch of the warp wires and between 19 and 21 wires per whole inch of the woof wires. The diameter of the wire should be 0.0165 in. and the average diameter shall not be outside the limits of 0.0160 and 0.0170 in.

The No. 30 sieve shall have between 29.5 and 30.5 wires per whole inch of the warp wires and between 28.5 and 31.5 wires per whole inch of the woof wires. The diameter of the wire should be 0.0110 in. and the average diameter shall not be outside the limits 0.0105 to 0.0115 in.

55. Immediately after mixing, the standard mortar shall be placed in the molds, pressed in firmly with the thumbs and smoothed off with a trowel without ramming. Additional mortar shall be heaped above the mold and smoothed off with a trowel; the trowel shall be drawn over the mold in such a manner as to exert a moderate pressure on the material. The mold shall then be turned over and the operation of heaping, thumbing and smoothing off repeated.

56. Tests shall be made with any standard machine. The briquettes shall be tested as soon as they are removed from the water. The bearing surfaces of the clips and briquettes shall be free from grains of sand or dirt. The briquettes shall be carefully centered and the load applied continuously at the rate of 600 lb. per minute.

57. Testing machines should be frequently calibrated in order to determine their accuracy.

58. Briquettes that are manifestly faulty, or which give strengths differing more than 15 per cent from the average value of all test pieces made from the same sample and broken at the same period, shall not be considered in determining the tensile strength.

XV. Storage of Test Pieces

59. The moist closet may consist of a soapstone, slate or concrete box, or a wooden box lined with metal. If a wooden box is used, the interior should be covered with felt or broad wicking kept wet. The bottom of the moist closet should be covered with water. The interior of the closet should be provided with non-absorbent shelves on which to place the test pieces, the shelves being so arranged that they may be withdrawn readily.

60. Unless otherwise specified all test pieces, immediately after molding, shall be placed in the moist closet for from 20 to 24 hr.

61. The briquettes shall be kept in molds on glass plates in the moist closet for at least 20 hr. After 24 hr. in moist air the briquettes shall be immersed in clean water in storage tanks of non-corroding material.

62. The air and water shall be maintained as nearly as practicable at a temperature of 21°C. (70°F.).

SECTION XXX

THE THEORY OF PLANT LOCATION AND DESIGN

By Henry H. Buckman[1]

Introductory.—To select and constantly maintain a definite *point of view* is the first duty of the designer. At first blush it might appear that the design of chemical engineering plants, owing to the multiplicity of the processes involved and the apparently highly specific nature of almost every case, is a subject impossible to treat as a coördinated whole. But a closer view of the field will disclose a remarkable simplicity of the underlying structure, obscured it is true, by an infinity of details, but everywhere yielding to a common system of analysis. The plant embodying truly *unique* features is rare indeed. The exchange of a given amount of energy between given masses of material with corresponding increase of entropy of the system involved; the whole covering given changes of time and space—that is the whole of any art. Our methods of causing, controlling and measuring such changes are rather less than more than enough to cause embarrassment to the engineer.

In order intelligently to select his point of view, it is absolutely necessary that the designer give a large amount of study to certain general aspects of the field within which his design is expected to function. Too much stress cannot be laid upon the preliminary study. The success or failure of a design will certainly depend upon it. Luck seldom favors the careful designer and never the careless one. Yet the number of really unknown conditions surrounding all ordinary materials, insofar as they affect practice in the arts utilizing those materials, is surprisingly few. The steps by which the designer may achieve the comprehensive point of view so necessary to a true design are so plainly indicated as to leave little excuse for a failure to meet and provide in advance for all conditions likely to arise. It should be remembered that that design is a failure which condemns a given amount of capital to turn over and over in a groove without a chance of return, just as much as is that set of blue prints and specifications which commits so much labor and material to the scrap heap. Both are graveyards for capital.

Those general considerations which govern the detail of all designing work, and which the designer must thoroughly study before proceeding to formulate his plans at all are the following:

1. The nature of the investment.
2. The nature of the industry.
3. The type process.
4. The location: geographic, topographic, economic.

When the designer has accumulated all available data under these four general heads, and has thoroughly digested the significance of each point developed, he will be in a position to view his enterprise as a whole, and his ability to do this will indicate his caliber as a designer.

[1] President, The Buckman Corporation, Jacksonville, Fla.

Up to this point the work of the designer is assimilative. From this point forward, the work becomes creative, and necessarily enters the phase of detail. This should be thoroughly systematized and subdivided. The following system is recommended as representing the minimum of care and division allowable, and yet one which, conscientiously followed, should insure a successful design. Each division should be studied in turn, and each with reference to all the others. In the order recommended they are:

Type of construction.
Influence of separate related units.
Control.
- (*a*) Administrative.
- (*b*) Labor,
- (*c*) Time and material,
- (*d*) Temperature and moisture, and
- (*e*) Light.

Power distribution.
Waste and by-product disposal.
Sanitation.
Hazards and insurance.
Storage.
Drafting the design.

Each of these subdivisions is treated in more detail in later paragraphs. We return now to a detailed consideration of the four fundamental general aspects governing design, the first of which is:

The Nature of the Investment.—That the nature of the investment itself should be the fundamental governing factor in all plant design seems a fact too obvious to be mentioned, but experience has shown that this supposedly first principle of commercial design is more often violated than is any other, and to this fact is due a large percentage of failures. The engineer should bear in mind that the primary object of the plant he is to design is to return earnings on a certain investment—the making of a product must always be a secondary object, no matter how important. When this ceases to be the case, we have almost invariably failure of both earnings and product. It is only necessary to consider the course of certain war-time engineering activities to find ample illustration of this.

The engineer is essentially an economist,[1] and he is a poor engineer who loses sight of the fact that the plant which he is about to design is simply an unavoidable detail in achieving the main object of his activity—the creation of wealth. He should keep constantly before him not only the size of the investment proposed, but the entire scheme of financing. He should know and weave into his design the rate of interest demanded, the number of years allowed for amortization of any proposed debt, the net earnings expected, and the number and general character of the securities of which the proposed plant will be the physical basis. Each of these factors should be carefully considered, and only that design is well conceived which gives due regard to all. Just as the relation of working capital to plant investment would govern the design controlling goods in process, so should the amortization period and depreciation factor influence the choice of construction type and materials. And so with all these factors—each will be found to govern some one or more vital detail of the design,

[1] An old definition of an engineer was "one who could do with $1 what any fool could do with $2."—EDITOR.

and when he finds that he cannot square the design with their demands, the wise engineer realizes that he has been attempting the commercially impossible.

A proper appreciation of the nature of the investment is impossible without due consideration of the *scale of projected operations*. All industrial processes have an optimum scale upon which they may be carried on. More important still, all have a *minimum*[1] scale upon which they can be profitably engaged in. Minimum, optimum and actual proposed scale of operations should therefore be first of all determined by the designer, and set up as a guide in all subsequent decisions.

Nature of the Enterprise.—After the nature of the investment has been considered, the next most fundamental point which should engage the attention of the designer is the nature of the enterprise itself. By this is meant the general type of the industry in which the proposed design will function; whether public service or private; whether a well established process with an accumulation of standard practice behind it, and if so, whether it represents a large or small class of producers, or whether the proposed design represents a launching into a more or less untried industry, where the unexpected is certain to happen.

Regardless of the nature of the product to be dealt with, a design expected to function in public service is surrounded by more rigid limitations than is the design for private service. With public-service designing, permanency of construction and efficiency of operation invariably take precedence over first cost, while in private service, the reverse is often properly the case. On the other hand, both topographic and geographic location of the public-service design very often inject factors into the designer's problem which should seldom, if ever, appear with good reason in the case of private service, where the designer is usually free to exercise his prior judgment as to location.

The question as to whether the enterprise represents a small or large class of producer is one which the designer should consider most carefully. The smaller the class, the more important becomes the factor of location with all its attendant conditions. In any event, and especially if the class be a large one, the designer will do well to select from all available examples the best type of construction and arrangement as proved by experience. Too often, this obvious mode of procedure is violated by the designer.

Whether from unwillingness to recognize the value of the experience of others, or from sheer infatuation with certain ideas of his own, there are frequently found incorporated in a design details which other plants have long since proven inefficient or inoperable; all of which a careful study of the field would have brought to light. It has been said, and with considerable truth, that whereas the number of new and good ideas yet to be conceived and tried out is legion, on the other hand, all possible mistakes have already been made. The difficulty probably lies in the fact that while successful practice is common knowledge, the man who has made an expensive mistake usually considers it as his personal property. Even so, there is very little excuse for mistakes in design in standard practice. That mistakes are numerous and that they are made over and over again is due chiefly to the failure of the designer to investigate the mistakes of existing industries of the same kind.

Some latitude must be allowed the designer in a new field, but even here, the only legitimate excuse for failure of the design is unavoidable ignorance of certain characteristics of the materials themselves, which develop only after the design is complete. Modern chemical engineering methods have been so standardized that, given a complete knowledge of all the chemical and physical constants of the materials to be

[1] As interestingly pointed out by J. R. Finlay in his discussion of the Utah Copper Co's. scale of operations.

treated, the designer has only to select known processes best fitted to these constants. A critical examination of mistakes in chemical engineering design will usually show that failure is the result of the designer's not allowing for the behavior of a certain material under certain conditions—behavior which could have been predicted in nine cases out of ten.

When the contemplated design is in a new field, this study of the physical and chemical constants and characteristics of the materials and products becomes pre-eminently important. If these constants are not known, they should be determined with the greatest care before the designing work is begun. These should include specific gravity, viscosity, behavior toward moisture and behavior under varying temperatures, and varying conditions of light, magnetic and static charges; critical angle of fall both wet and dry, hardness, friability, heat and electrical conductivity, solubility, specific heat, latent heat of vaporization, behavior in storage, results of friction, influence of pressure, etc., etc., of both original materials and intermediate and final products. It is a vicious mistake, but one made only too often, to assume that because the new material to be dealt with has superficially the character of, say, a syrup, that it will behave like a syrup; or because it has apparently a sandy nature, that it can be handled as such.

Type Process.—There are but five types of process involved in any chemical plant. These are *transporting*, *energizing*, *reacting*, *separating* and *conditioning*. The innumerable details and subdivisions under these five heads constitute proper subjects for machine design, but they have no place in the general subject of plant design. Plant design is the physiology of an industry; machine design is its anatomy. Plant design deals with the correlation of functions, machine design with construction and work. In order, however, that the designer may keep more clearly in view these five processes and their government of his design, they may be approximately delimited as follows:

Transporting	Separating	Conditioning	Reacting
Rail, cable and other ways	Filters	Grinders	Vats
Drags	Dryers	Crushers	Tanks
Elevators	Separators	Briquetting machines	Smelting furnaces
Conveyors	Collectors	Mixers	Cells
Pipes	Stills	Shredders	Combustion chambers
Pumps	Skimmers	Digesters	Retorts
Chutes	Sifters	Rolls	Roasters
Feeders	Settlers	Atomizers	Energizing
Conduits	Strainers	Sprayers	Heating equipment
Ditches	Extractors	Gasifiers	Cooling equipment
Conductor wires	Dewaterers	Compressors	Exchangers
Loading and unloading machines	Centrifuges		
Canals	Flotation apparatus		
	Wet tables		
	Evaporators		
	Presses		
	Non-chemical precipitators		
	Sizers		

With these five major processes in mind, the designer should weigh carefully the various phases of the proposed industry as affected by each, and he should clearly determine and set down in their order of importance the relative position of these

processes. By importance, should be understood not the numerical frequency or preponderance in the enterprise of one of the five major processes, *but that process involved which represents the greatest percentage of the production cost* (all things considered). The consideration of a few specific instances will not be without value. In the manufacture of sulphuric acid, dyestuffs and rubber goods, reaction processes are the governing factors in design. The design of plants producing cereal products, glue and glass will have conditioning processes as the limiting factors. The production of steel and fertilizers represents chiefly design in transportation processes. Carborundum and graphite call primarily for attention to energizing processes. Thorium nitrate and salt production have *separation* as their type of process. The failure to recognize the type process represented by a proposed plant is one of the most fruitful and common sources of error in design.

Not until the designer has settled clearly in his mind this question of the type processes involved; not until he can vision a clear picture of the relative places to be occupied in his design by each type process (using always production cost involved as the criterion of importance) is he prepared to proceed with the next fundamental consideration which will govern his design, namely location of the plant.

Location.—Three phases of the location of the proposed plant will influence the design. These are *geographic, topographic, economic.* Upon the geographic location will depend to a considerable extent the materials of construction, the rain, snow, ice, heat, wind, sunlight and moisture protection and accommodation features. This refers to physical limitations imposed by climate and other truly geographic factors.

In all locations reinforced concrete is probably the best of all materials for permanent structures, where the height does not exceed 80 ft., and where the foundations do not enter salt water. For less permanent construction, the choice lies between galvanized and black iron for roofing and sheathing, and between steel or wooden framing. In the case of wood, there is the choice of treated or untreated materials. The economic factors enter so largely into these selections, that it is better to view the geographic factors as being of a negative and limiting type. In general, it may be said that for plants located between 35° N. and 35° S. latitude, except for the most temporary structures, the less wood used the better. In higher latitudes, where bacterial action and sun effects are less acute, and where the question of excessive sweating makes iron structures objectionable, wood may well be the predominating material. As between galvanized iron and black iron, the former is always the best practice, except for plants located below 35° latitude and on the seacoast. Here, experience has shown that well-painted black iron will outlast the galvanized material. This applies to pipes and fittings, as well as to sheathing. It should be borne in mind that wherever great humidity and marked changes of temperature are consistently present, the designer must expect metal roofs and walls to sweat at intervals, and this may have very serious results on process or product. Sweating of the roof is particularly to be guarded against.

The question of nails and general ironing should be very carefully considered with regard to geographical location. In low latitudes near the seacoast, galvanized nails and irons should always be specified. In studying the geography of the proposed location, particular attention should be paid to rainfall and snowfall data. This is especially important in the case of roof design.

Below a latitude of 30° and an altitude of 400 ft., the designer need make no special provision for ice. Above this latitude and altitude, however, this feature becomes of paramount importance. The designer must allow for protection of all liquids and gases and associated service apparatus in storage, process and transit, for the contrac-

tion of all parts other than wood, for mechanical failures due to loss of friction from ice coatings, for mechanical strains due to weight of accumulated ice and for the increased accident hazard to employees. The design of piping systems is too large a subject to be more than touched upon here, but it may be well to call attention to a few of the more important points. One expansion joint for all straight runs of above ¾-in. size is necessary. Wide-angle elbows on all steam and other piping are recommended where intermittent pressures are likely to obtain, or "water hammer" to develop. All automatic valves need especial protection. Few such will fail to give trouble if unprotected from low temperatures. Especial care should be taken with the layout to avoid "traps" which will not drain automatically. Wherever possible, all gravity return drains should be given a pitch of not less than ⅛ in. to the lineal foot. Flexible hangers should be used in all cases. Close return bends and straight ells should be avoided wherever possible. Whenever there is a choice, piping should be on interior south walls, or overhead, when the design calls for more than one story. When only one story is contemplated, placing the great valve of the permanent supply pipes below the floors and beneath the frost line is often well worth the additional cost. In any event, pet cocks for bleeders and stop-and-waste cocks should be plentifully supplied in all lines. Flanged-joint piping and fittings must be particularly guarded, and especially should the designer avoid curves and offsets in this variety of piping, unless special flanges are used. Expansion washers should be allowed on all flange bolts.

Expansion joints in all horizontal concrete surfaces should be provided. Such joints should pierce the entire thickness of the concrete floor or other surface, and should be from ¼ in. to ⅜ in. in width for sections not exceeding 10 ft. in length along the line of expansion. Asphalt, gilsonite and lead wool are the best fillers for such joints. Concrete floors, platforms and steps should all be designed with a minimum slope to drains of $\frac{1}{16}$ in. to the lineal foot, and "dips" and depressions carefully avoided. If such surfaces are to be exposed to more than an ordinary amount of ice, the use of thin finishing coats should be avoided.

In connection with the geographical location of the design, temperature records of the locality should be carefully studied—daily, monthly and annual means, minima and maxima. In localities subject to extremely high temperatures, all-metal sheathing and roofing is usually to be preferred to wood. In such locations storage should not be provided or contemplated in lofts directly beneath the roof, unless very inert materials are to be stored. Temperatures of 140°F. are not uncommon in such conditions, and must be experienced to be appreciated. The overhang width of eaves is worthy of attention in this connection. Nine to 18 in. will suffice in temperate latitudes, while 18 to 36 in. is recommended for lower latitudes. It is the duty of the designer to eliminate as far as possible by the fundamentals of his layout the necessity for temperature control.

Mean and maximum wind velocities should receive careful attention. Likewise, the direction of prevailing winds should be noted and taken into account when orienting the plan. Fire doors of boilers and furnaces and doors of all chambers where hot or finely divided materials are handled should whenever possible be placed to the leeward. The same holds for drying-room doors, and doors opening to rooms where gravity feeds of light materials are used. In many geographical locations the maximum velocity of the prevailing winds is the limiting factor in the height of structures. Wind pressure should be carefully studied and allowed for.

When studying the geographical location, relative humidity records should be carefully taken into account. Many processes are vitally affected by moisture in the air, and without artificial conditioning of the plant atmosphere, it is frequently impossible to operate both night and day shifts owing to the greatly varying humidity in some localities.

In designing all refrigerating or supercooled systems, it is especially necessary to study the geographical location in connection with the relative humidity records. Excessive humidity is often a most troublesome factor, and in some localities may become prohibitive.

In introducing internal combustion engines into the design, due allowance must be made for humidity as controlled by geography. This is not only from the point of view of efficiency, but by actual operability. Locations which experience prolonged fogs are not adapted to internal combustion engines using low-grade fuels, and if gasoline is not available, the designer will do well to provide a source of dry air for combustion purposes.

The economic location of the proposed plant may profoundly influence the design. The economic location is determined by supply of materials, power and labor on one hand, and markets and competition on the other. A plant located far from its source of raw materials must have included in its design much more ample provision for storage of raw materials than when such are close at hand. The same is true of fuel. When purchased power is used from only local source of supply, and continuous operation is essential, auxiliary units should be provided, if the size of the operation and the cost of a shutdown will justify it. If more than one source of purchasable power is available provision should be made for utilization of an auxiliary source in emergencies. If labor is scarce it is often good designing policy to increase the ratio of machines to men, and perform all operations on one shift. With a plentiful supply of labor, it may be cheaper to substitute men for machines, and design a plant to operate two or three shifts on a lesser number of machines. The important point is that the designer should know and decide upon this feature in the beginning, and mould his design accordingly. Markets and competition often effect the design. It is often not sufficient to produce goods of a given chemical analysis or character. They may, owing to existing market demands, or criteria developed by competing products, have to be sent to market in a given physical condition of form, color or consistency, or a special form of packing. These factors should be well considered and allowance made for them in the design.

The most important factor in the economic location of a plant as it affects the design, is the situation with regard to transportation. Here, the scale of the operation is the governing factor. It is too often assumed that a location affording water transportation is preferable to one affording rail shipments, and in many cases the conclusion has been an expensive one. If the raw materials to be brought in or the finished products to be shipped out are handled in quantities equal to cargo shipments, then facilities for water transportation become of paramount importance, for not only are cargo shipments of raw materials and finished products certain to be at a lower rate than car shipments by rail, but the added advantage of bringing in fuel in cargo lots can be enjoyed. On the other hand, for enterprises where the incoming and outgoing shipments are in less than cargo lots, it may very well be that rail shipments even at considerably higher cost are much to be preferred. A small lot of say, 15 to 30 tons of material can be loaded into a car in bulk, and enjoy all the advantages of bulk loading and unloading as well as escape the cost of containers. Even when containers must be used, the material itself usually sets the limitations on the nature and cost of these.

As opposed to this, less than cargo shipments by water offer conditions which often prove troublesome; *i.e.*, the necessity for a regular service of bottoms engaged in the general carrier trade, the usually more strict and expensive regulations as to con-

tainers, the general impossibility of making less than cargo shipments in bulk, the infrequency of sailings as compared with railroads, and the necessity for transhipment at destination. The tonnage involved in the proposed operations will usually decide which location, rail or water, is the more advantageous. The ideal location will afford access to both, and in such case the designer should always make his layout and orient his design so that either means of transportation can be used, even if he never intends to use but one. This ability to divert, on short notice and at little expense, the flow of shipments from rail to water or *vice versa*, will be the most potent of all factors in establishing and maintaining favorable commodity freight rates on the raw materials or finished products under consideration.

The topographic location of a plant is perhaps the most important of all location factors in the design. Upon the skillful utilization of topographical features will depend the construction cost and the efficiency of the system of transportation of material into, through and away from the plant. The reader is here referred to the paragraph on "Type Process." If the plant to be designed has transportation for its type process, then the utilization of topographical features toward economical transportation becomes the chief duty of the designer, and all other considerations must be subordinated to this one. If the type process represented is one of the other four enumerated, the question of transportation becomes of relative importance, the degree of which must be decided in each individual case. Here we come upon the familiar question as to the relative desirability of the "hillside" type of layout as compared to the "broadcast" design. As regards plants where the type process is transportation, there can be little doubt that the "hillside" type of design is not only the more desirable but is vital to success if competition in production costs has to be met.[1]

As stated above, in other type processes, the question must be answered in each individual case, the answer depending solely upon the degree of importance of transportation in the design. In every case, it is well to remember that the cheapest and easiest way to move any substance from one place to another is to allow it to roll downhill. Likewise, the cheapest and most convenient way to get large quantities of any solid material up hill is to haul them up in standard railway equipment. In other words, it may be assumed that the "hillside" type of design (whether actually located on a hillside, or having hillside conditions in a measure counterfeited by altitude of structure) is in general the economical type for chemical-engineering plants, and that the fairly numerous exceptions to this rule are the results of special features of the process or location involved which more than offset the transportational disadvantages of the "broadcast" type.

Type of Construction.—From the point of view of the chemical-plant designer, there are but two main types of construction, *wooden frame* and *steel frame*. These may be subdivided as follows:

Wooden Frames	*Steel Frames*
(*a*) With wooden walls and roof.	(*e*) With wooden walls and metal roof.
(*b*) With wooden walls and metal roof.	(*f*) With masonry walls and metal roof.
(*c*) With metal walls and metal roof.	(*g*) With concrete walls and metal roof.
(*d*) With masonry walls and metal roof.	

[1] This type of design is especially well exemplified by many of the Western lead- and copper-smelting plants.

The type to be adopted depends upon a great many factors, chief of which are the type process, the nature of the investment and the location.

Examples of each type to be found in good practice are given below:

(*a*) Canning factories, drying and curing sheds, mining mill buildings, and numerous others which serve chiefly as shelters for machinery or operations in comparatively removed locations.

(*b*) Same as class (*a*) but in the warmer climates where the usual objections to metal roofs do not obtain.

(*c*) Smaller foundries and metallurgical mills where overhead traveling cranes are not used; Naval stores and textile warehouses, usually confined to one story structures.

(*d*) This class represents a compromise between the hazardous and the fireproof types, and is often termed "slow-burning" construction. It probably more generally meets the demands of the average designer than does any other type. It has much to recommend it, and numerous examples of almost every type of industry will be found utilizing this type of construction. It is not, however, recommended for plants over two stories in height.

(*e*) Many foundries, alloy and heavy chemical plants employ this type. The steel frame gives fire protection and supporting strength for cranes and other heavy fixtures which cannot be directly supported from the floor, and at the same time affords no sweating of walls—often a most objectionable feature. This type is slowly gaining in favor and has much to recommend it for single-story work.

(*f* and *g*) These types are the ideal structures for long time investments, and for type processes requiring more than two-story elevation.

Influence of Separate Associated Units.—Careful consideration of this factor is necessary throughout the design if the plant be composed of more than one building or if it is one of a number of plants engaged in working up the same material. In the former case, if the type process is transportation, the location of buildings should conform as nearly as possible to the physical flow sheet. This is not always the best practice in other types however, where control or conditioning may be the guide to location regardless of transportation. While the uninterrupted flow of material from process to process is always the ideal condition to be obtained, it is often good strategy to arrest or even reverse the direction of flow under certain conditions where transportation is of secondary importance. This fact makes necessary a most careful survey of the influence of all units in a plant upon each other before definite location of each is decided. For example: in a process which requires natural sunlight for control of the product by the workman, separate units must be located so that in flowing from one to the other, the material will pass, or lie to the north or west of the workman, regardless of transportation difficulties.

Again, if the material requires retreatment at any stage, it must not be allowed to get too far away from the unit constituting the treating equipment in question. In all cases where retreatment is practiced, intermediate storage units should be provided to take up the surges in the flow always consequent on interruption of the process from any cause. The more frequent or lengthy these interruptions are likely to be, the larger should be these intermediate units. While they condemn perpetually a certain additional amount of capital to "goods in process," this is often more than justified by continuity of output. The designer should beware of a flow sheet too

tightly and rigidly knit together. In such a case interruption at one point causes a surge and loss of control throughout the entire process. These surges result always in loss of time and usually in loss of material. Proper attention must be given to the location of intermediate storage depots between the more important steps of the flow to serve as elastic units to absorb the surges.

Control.—Provision for successful control is the keynote of success in designing. Systems of control superimposed on already existing designs are never entirely successful. The original design must embody the elements which make efficient control not only possible, but not too expensive. Without proper provision for control, proper departmentalization is impossible, and cost accounting becomes involved and inaccurate. Modern accounting is merely a comprehensive system of control. With proper designing in the first place it becomes a real tool which the management may keep constantly in use to lower costs and raise production. Otherwise, no available system of accounting is anything more than a record.

Administrative control should be provided for in the design. This includes the proper allowance for the activities of all administrative labor from the chief executive down to the foremen. Due attention must be paid to the actual difficulties opposed by time and space to close coördination. Other things being equal, the best design is that which places the administrative labor in closest proximity to the processes being supervised. Despite the numerous instances of widely separated plant and office, it can be shown that where one plant only is under consideration, the most efficient and least expensive administrative control is possible when the entire office of a plant is located at the plant itself. Further than this, the office should be centrally located at the plant as regards to flow sheet. Only where one office is called on to control several widely separated plants, is it justifiable to locate it at a considerable distance, and this always entails expense. The most modern tendency is to swing away from the combination with a "downtown" or city office, to that design which places the entire administrative control at the plant itself.

Control of labor should be most carefully considered in the layout. The ideal control will place the laborer at his task immediately after his time is chargeable to the company, or in other words, as soon as he punches the clock, and will remove his name from the payroll immediately upon his laying down of his task. This is never entirely achieved in actual practice, but a good design will provide for its practical realization. The physical control of labor is best obtained by proper departmentalization, and then by adequate fences and barriers, with automatic devices for recording the passage of laborers from one department to another. A man-tight fence around the entire plant is most desirable. Ingress and egress of all labor should be restricted so far as possible to one gate. The ideal design should preclude the admission of a laborer to the precincts until after he has punched the clock, and should allow of a direct, supervised route from the clock to the job, and return, and the laborer should be removed from the precincts immediately his time ceases to be chargeable to the company. If company dining rooms, rest rooms, etc., are included in the design, they should be beyond the time clock and outside the precincts. Pay windows, commissaries, wash rooms and employment offices should be similarly located. The location

of toilets necessarily within departments should be most carefully considered. They should be close to the job and within sight of the foremen. The amount of labor lost in toilets is usually 1 to 2 per cent and may greatly exceed this figure unless proper supervision is possible. Proper provision for drinking water is an economy in design. Men work better and less time is lost in going to the tap.

Control of time in the design is the next most important feature after control of labor. It is next to impossible to make this control too elaborate—for it embodies not only time of labor but time of process and time of capital. Time control is obtained by two general methods, both of which are necessary. These are control by record and control by observation. Let the designer remember that no device, human or otherwise, has ever improved on the clock for telling time. Estimated time in process work should be forbidden just as much as it is in labor time. Two complete sets of clocks are advisable. One of these is for automatic record and the other for observation. The former are for the use of all labor according to circumstances. The latter are for foremen only. Time control should center in the plant manager's office. The use of master clocks with electric standardization is recommended. The proper location of both recording and observation clocks is most important. Observation clocks should be placed in every department, and should be large enough and so located as to be visible from every part of the department. All should be synchronized and controlled by a master clock. Wherever human time-keepers are employed, provision for the control of these automatic clocks should be made. It is recommended that the designer employ clocks freely. It is difficult to err in this direction, if the clocks are standardized and under electric control of a master clock. The continuous proper speed of flow of material is absolutely dependent on clock-controlled labor and machines.

Control of material is achieved by control of volume and control of weight. Ultimately the former is always resolved into the latter. The proper types of volume- and weight-control devices is a subject belonging properly to detailed construction, to which the reader is referred. At this point only the general subject of control is considered. The designer's guiding principle should be the fact that in the vast majority of processes (as a practical matter due to limitations of the art) the materials handled change both in volume and weight as they proceed through the flow sheet. The amount of material control desired will depend on the system of cost accounting selected. The simplest case is where only weights of incoming and outgoing raw material and finished product are required. From this case to the most elaborate control we have an infinite gradation of complexity. The designer, with his accounting system in mind must decide to what extent it is necessary to carry this control. Here, unlike the case of time control, it is easily possible to overdo. Generally speaking, it may be said that the minimum requirement is sufficient control to permit an accurate knowledge of raw materials (including fuel) on hand, goods in process, and finished product. Practically this entails car and platform scales for incoming and outgoing material, and platform or hopper and automatic scales for goods in process. The designer's task here is comparatively simple, though important, and consists chiefly in, first, determining the number of weighings or measurings demanded by the control in view, and then the proper location of the weighing or measuring devices, with due regard to economy of time and labor in getting the material through them.

Control of temperature applies to both plant and process, and is secured along two general and somewhat different lines. Broadly speaking, control of temperature in the plant is a control of atmospheric temperature within the plant buildings. Control of temperature in the process is the control of temperature within the material itself. Not infrequently the two conflict rather sharply, and the amount of control necessary and the means to be employed in both cases should be scrutinized with care. Control of atmospheric temperature within the plant is best secured by central heating units, when the temperature is to be maintained above that of the outside air, and by proper ventilating systems when the temperature within is to be kept down to that of the outside air. No really practical method of atmospheric-temperature control has yet been devised which will permit of any considerable, continuous lowering of the atmospheric temperature within the plant below that outside. This is because of the inevitable throwing out of moisture by cooled air, and the consequent dampness of all things in the supercooled area. But by the proper utilization of artificial and natural draughts and shading, a degree of comfort for the workmen can be achieved which is eminently worth while. As this comfort is dependent largely on increased evaporation of moisture from the skin and not on decreased temperature, the designer will do well to content himself with providing for perfect ventilation and then turn his attention to possible moisture control.

The maintenance of higher temperatures within the plant than obtain without is subject to more positive treatment. Of the two general systems of plant heating; that of bringing the heat directly to the air of the plant, and that of first introducing the heat into the air and then bringing the warmed air into the plant; the choice is largely governed by the type of construction under consideration. Buildings of wood, and particularly buildings of shed type and all lightly or loosely built structures require direct heating from radiators, salamanders, or hot air blasts. It is difficult and expensive to attempt systematic atmospheric conditioning in such structures, and the designer should use care not to make his temperature control more elaborate than his type of construction or his climatic conditions will justify. Where buildings are of steel and concrete and tightly constructed, there can be little doubt of the superior desirability and efficiency of heating and controlling temperature by properly conditioned air. In certain climates, a careful weighing of this fact should be allowed to influence the choice of type of construction within reason, especially if the labor element in the process is large. The optimum atmospheric temperature at which human labor should be carried on is that which will throw the least work on the temperature control system of the human organism itself. Obviously this will vary for different forms of labor and for different atmospheric conditions.

It is probable that the human laborer is most efficient when there exists the best balance between the work required of the skin, the kidneys and the lungs, and this should be the balance sought in control of plant atmospheric temperatures. When his type of buildings permits the use of conditioned air, the designer can do much to increase the efficiency of his design by careful consideration of these facts. When the type of construction necessitates direct heating, he will do well to confine his efforts to provision for ample heat and rely on properly conducted outside atmosphere to achieve as much control as is possible under the circumstances. In all cases, recording thermometers are called for to the extent that the record can serve as a basis for control. Seldom is the control so slight as to make the use of recording thermometers unjustifiable.

The control of process temperatures is a local problem and belongs more to

the constructor than the designer. In general, it may be said that recording thermometers are almost always to be preferred to merely indicating instruments. Of the three types (neglecting the fusion thermometers or cones used in the ceramic industries), *expansion*, *thermo-electric* and *radiation*, the first is preferable wherever it may be employed. Thermometers of this type are more accurate and more positive and will outlast the other types. At temperatures or distances where the expansion thermometers cannot be employed, the thermo-electric types are recommended. Their chief advantage is the feature of recording at relatively great distances. Radiation thermometers are useful at temperatures where other types cannot be employed, but the field in which they can be accurately employed is limited. They have also the drawbacks of the personal equation and the lack of a recording feature.

Control of moisture like control of temperature, is sought both for general plant atmosphere and for atmosphere of the process chamber. In the former case, much that has been said relative to atmospheric-temperature control applies here also. Only in tight, well constructed buildings should this be attempted. When the type of construction will permit, however, it is usually good design to provide for the most careful control of this factor. The only feasible method of drying air on a large scale is to chill it and cause a precipitation of a part of the contained moisture. Moist air is produced by the direct addition of moisture. As it is impractical to carry out either the drying or the moistening process within the rooms occupied by workmen or processes, the usual method is to maintain a balance between moist and dry air by introducing to the plant air already conditioned both as to temperature and moisture and then providing for a continuous flow of this atmosphere through the plant. Control is thus secured, and is indicated by psychrometers. Satisfactory recording psychrometers are not available, and control must be maintained by indicator readings, taken as often as necessary. Here, as in the case of temperature, the optimum humidity is that under which the temperature control of the human body will have the least work to do. This is also obviously dependent upon the nature of the labor, and no hard and fast rule can be laid down. The fundamental fact to be kept in mind by the designer here is the same as in the case of temperature control, namely, that the normal temperature of the blood is 98.6°F., and that the normal temperature of the outermost skin surface is considerably below this point. The difference represents the working margin of safety allowed the organism to control the temperature of the blood and exercise the excretory functions. Advantage may be taken of this within certain narrow limits, and increased moisture substituted for increased temperature and *vice versa*—but it should be realized that optimum temperature is a more or less definite point and that maintainence of comfort by the body at temperatures away from this point by the aid of increased or decreased moisture is only achieved by work of the organism itself through its temperature-control devices. Hence maintainence of comfort need not necessarily mean maintainence of healthy efficiency.

The control of moisture in the processes themselves is achieved in the same way as in general plant atmosphere. There is one exception to this, and that is where moisture is continually contributed to the atmosphere of the process chamber by the material itself, and where the necessities of the process make it impossible to remove this by chilling the air or by mechanical removal of the atmosphere itself, if it be other

than air. In such cases, direct drying by lime or other moisture absorbing substances is called for.

Control of light includes the control of both artificial and natural light. The control of natural light is brought about by proper coloring of walls and ceilings, and by properly sized and shaded openings. It is better for the designer to exercise his talent on these points in the first place than to be obliged to make up for deficiencies in design by an unnecessarily elaborate artificial lighting system. Where wall space is not actually required for apparatus, the modern tendency is more and more toward large windows and many of them. The advent of wire-filled glass and steel-framed windows has made this possible on an increased scale. It should be borne in mind, however, that ordinary transparent glass is a poor reflector, and that rooms with a great window surface of plain glass are correspondingly difficult to light from within by artificial means. The use of a light frosted glass serves as a compromise between day and night requirements.

Walls, ceilings and, wherever possible, fixtures should be painted white. It is safe to assume that provided it is properly diffused, there is no danger of getting too much light. Wherever the use of white paint is impractical, the next lightest color should be used. Black is a very inefficient color from a lighting standpoint, and almost any other color is preferable. For artificial lighting, the question as to which is the better, monochromatic or polychromatic light has not been completely answered, but the present concensus of opinion leans decidedly toward the use of ordinary "white light," either produced by the tungsten filament or the incandescent gas mantles. For special purposes or highly specific processes, the light of the mercury-vapor arc may prove more satisfactory. Under our modern conditions, the designer in arranging light control has only diffusion and reflection with which to work. Generation of light itself has become too much standardized to permit of any special adaptations for specific designs. Diffusion is merely compound reflection, so the problem resolves itself into two very simple elements; the selection of angles, surfaces and distances in the form elements of the design itself and the selection of materials with the highest practical albedo. There can be little doubt that the semi-indirect system of lighting is usually preferable. Reflectors should be translucent, in order evenly to diffuse the light and prevent shadow zones. It is a mistake to illuminate only the plane of work, except in isolated cases. Individual illumination of special work is a function of construction, not of design.

Distribution of power is properly regarded as one of the major phases of designing and usually comes in for its full share of attention from the designer. Unfortunately the true theory of power distribution is often imperfectly understood, and elaborate plans do not always bring efficiency. Briefly stated; it is cheaper and often more practical to transmit power than it is to transfer material. The tendency of the mechanical engineer, with his mind centered on the most efficient and economical generation, transmission and application of power, is too often to subordinate to this the even more important flow sheet or general process. The distribution of power like all other factors in the design must be guided primarily by the type process—after that by the layout limitations of the flow sheet. It is a mistake to attempt to warp either of these to fit any arbitrary scheme of power distribution, regardless of how efficient.

From the above, it necessarily follows that the ideal system of power distribution is the most elastic, and there can be no question that this is at present the electrical system. It does not necessarily follow however, that the electrical system

is in all cases the most expedient, the most economical, or the most efficient. The nature of the investment, the nature of the industry, the type process and the location all have to be taken into account. Hence, it becomes necessary for the designer to consider the several possible systems of power distribution. These are: (1) the generation of electrical power at a central prime mover, and distribution by electrical transmission to various motor drives. (2) The generation of mechanical power at a central prime mover and distribution mechanically by line shafts. (3) Division and distribution of the prime movers themselves.

Where operations are on a considerable scale covering a considerable period of time and where the requirements for the immediate future are definitely known, there can be little doubt that the first system is preferable. Its advantages are the practically unlimited elasticity of distribution over any operating area, economy of operation, high efficiency of transmission and low depreciation under normal conditions. Its disadvantages are high first cost, absolute dependence of the entire plant upon one unit or group of units, impracticability of gradually increasing the available power supply to provide for gradual expansion, and the often serious effects of surges when a considerable proportion of the total load is subject to violent fluctuations, such as those attendant on heavy hauling and excavating work.

Where fuel is cheap and plant area not too great, the second system may very well become the most desirable. This is especially the case in certain types of industry or certain special locations. The chief advantages of this system are the ease and positiveness of operation, the low first cost of installation when compared with the first system, and the ability to absorb heavy surges. Its disadvantages are its greater cost of operation, its decreased efficiency of transmission and greater rigidity as regards distribution.

The third system represents a compromise class, when the first system is not justified by the nature of the investment and the location, and the second is made impossible or undesirable by the area covered by the plant. Such cases are not uncommon, but they can never show the low production costs of the first or second systems. The fundamental feature which usually justifies the adoption of this third system is too small a scale of projected operation. Here the designer is thrown back on the nature of the investment itself and the fact that this will not permit of the adoption of the first and second systems may often (although by no means necessarily) serve as a danger signal to indicate the fundamental weakness of the enterprise itself—due to the impracticability of the proposed *scale* of operations.

Waste and By-product Disposal.—All material which is not included in the regular product of the plant, and which is chemically or physically altered as a result of the operation of plant processes is either by-product or waste, depending upon the presence or absence of earning power. If the material thus altered is subject to profitable utilization or disposal, it is by-product; if not, it is waste. In either case due provision in the design must be made for disposal, whether profitable or otherwise. If by-product, this provision must take the form of storage, and transportation to market exactly as in the case of the main product. If waste, provision must be made for the cheapest possible disposal, otherwise the item of transportation will add direct cost to this indirect cost item. If the waste is voluminous, its disposal may often prove as important as any question to be decided by the designer. Solid waste which cannot be burned or otherwise consumed, may be either stored on the premises or removed beyond the plant precincts. In either case the problem presented is simply one of handling and transporting solid material. On the other hand, if the waste be liquid or gaseous, it

should be borne in mind that ultimately it is impossible to store it on the premises. It must eventually trespass on the property of others, both public and private. If the waste is of such nature and volume as to permit of this trespass without the objection of the property holders or the general public, no problem is presented. But if such trespass is objectionable or is likely to become so, then the designer has his work cut out for him. Here, his earlier study and analysis of the nature of the investment and the location will stand him in good stead. At best such problems are difficult. When certain legal restrictions exist, they are sometimes prohibitive for the industry itself.

Sanitation.—Broadly speaking the design must provide for sanitation from three points of view: (1) The effect of the plant on the public health; (2) the effect of the plant on the health of employees; and (3) the effect of employees upon one another. The first is less personal, less understood, and less likely to have attention demanded for it. For this reason it is usually most neglected by designers. It is, however, from a purely business point of view, well worthy of most serious consideration. A fundamental and not easily removed objection in the relations between any plant and the public health is as dangerous to the safety of the investment as are equally subtle and often ignored flaws in legal title to real estate or processes. They only need dragging into the public eye to condemn the particular investment with which they are associated. Increase of population is rendering the isolated plant more and more the exception, and the tendency of modern medicine is more and more to seek in great industrial enterprises the roots of menaces to the public health. Whether such menaces arise from the nature of the processes carried on, or spring from an unsanitary relation between the mass of employees and the surrounding public, it is much better to avoid or provide against these in the original design.

The effect of the plant processes on the health of employees is a subject which modern practice has reduced to fairly uniform procedure. Confinement and isolation of the objectionable process as far as possible on the one hand, and protection of the workman on the other constitute more or less standard practice. The endeavor should be, of course, to prevent entrance to the organism of the workman of harmful matter; the maintenance of normal atmosphere, light and temperature conditions and the avoidance of straining nerve and muscle beyond the elastic limit. The last, no less than the first two are secured by the design itself, for the policy which achieves the last is only possible in an adequately designed plant.

The effect of employees on one another as regards the health of each individual is largely a question of control and handling of excreta; gaseous, liquid and solid, and should be handled in the same way and with the same care as is the disposal of other waste. This practice has been reduced to a very exact science and there is absolutely no excuse for failure of the design in this respect.

Hazards and insurance bear a rather peculiar relation to each other. Both represent items of cost, one potential and the other actual. The cost of insurance is directly proportional to the degree of hazard. Aside from the absolute inherent hazards in the particular industry and type process under consideration and the hazard arising from the intellectual limitations of employees, the designer can absolutely control the degree of hazard and hence the cost of insurance. Hazards may be divided into two main classes: *human* and *natural*. Under the former heading can be classed *fire, explosion liability, burglary, mob violence.* and *war.*

Under the latter come *storm* and *earthquake*. It is instructive to consider that probably 95 per cent of all industrial losses come from human hazard and only 5 per cent from natural hazard. Yet this fairly represents the ratio of control of modern engineering over animate and inanimate nature.

It becomes evident that hazard depends upon control, and chiefly upon control of labor. There are two ways of attacking this problem, and the designer will do well to use both to the limit of his ability. The first is to remove as far as possible the human factor from the hazard by making protection automatic. Fireproof construction, sprinkler systems, self-acting alarms, safety valves, the housing of dangerous parts, etc., are typical examples of this method, and represent a constantly increasing tendency in modern engineering. This tendency is founded on the fairly well understood fact that the last factor to be brought under control of the plant design and the least reliable in its processes is the mind of the plant employe. The second method is to surround the activities of the employee with prohibitory equipment and regulations. Watchmen's pull boxes, no-smoking zones, etc., are examples of this method. The reader is again referred to the paragraph on control. Control is the essence of hazard prevention, and that design wherein control of labor and material is perfect will automatically exhibit the least degree of all hazards.

Design is Strategy; Construction is Tactics.—The engineer will do well to keep this difference clearly in mind. The actual production of design drawings from the first rough sketches to the finished blue prints requires the most careful method and systematic routine to secure results which are satisfactory. The difference between ordinary structural design and machine design on the one hand and plant design on the other is simply this: Ordinary structural design is in the last analysis a question of shelter from the elements; ordinary machine design is a question of pure mechanics, but plant design is a problem in coördination. There must be no loose ends, no blind alleys. Before the first ground is broken, the design must be complete to the last detailed drawing; the ground should further be accurately surveyed and staked to avoid errors in location. Structural drawings should be on a uniform scale of ⅛ in. to the foot.

No tracing should be allowed to be made until the original drawing has been checked by the designer and one other competent engineer. All calculations involved should be retained on original sheets, and these should be checked by the designer and one other competent engineer. The tracing may then be made, and must be checked and signed by the designer and the tracer. All tracings should bear a stamp carrying signatures of the designer and one other competent engineer under a statement that each has personally checked all calculations and drawing involved in that sheet. Drawings should be divided into three classes, and given a sheet and serial number accordingly—layout, detail and assembly. The actual work of designing should proceed in this order. The layout must be absolutely complete before detail and assembly sheets are begun. The next step after completing the layout is the making of the survey, and establishing of levels. Fills and cuts can then be calculated. The designer then locates his means of transporting structural material—usually a spur of standard-gage railway track—making this conform as far as possible with one of the tracks to be permanently used for the plant. The layout should contain in properly proportioned outline every space occupying feature of the plant and process.

Having located his construction track or tracks, the next step for the designer is to locate on his layout unloading, storage and handling depots for all materials of construction and mechanical units which will enter into the design. Especial attention should be given to allotment of ample room for lumber and steel stacks, with jib

cranes or other devices for economical handling. Warehouse room must be provided and accurately located for cement, plaster, and all materials which cannot be stored in the open. Temporary fire protection, watchman's call-box systems and (if deemed necessary) fencing, should all be provided for in the layout at this time, and not later. The economy of plant construction is achieved or lost in the drafting room, and is inseparable from the work of the designer.

One additional point of which every design should take account is the possible need for enlargement. This can be accommodated in the design by one of two methods; the unit group system and the individual unit system. The latter system provides for the addition of additional individual units to any given battery, by the necessary spacial arrangement of the original layout of that group or battery. The former allows of expansion by alloting proper spare ground space in the original layout for the construction of entire additional batteries or groups.

It is not to be expected that that design which fails to take in and allow for every detail of the process of construction itself will provide more perfectly for the process of operation. One is a good index of the other. The designer should remember that *charges against his process begin to accumulate with the very first time check of the first man employed in construction*, no matter in what preliminary capacity, and there is no possible way in the future of avoiding or unloading these charges. They are more permanent than the plant itself, and will always stand as offsetting entries against the efficiency of the design itself, for they represent truly the load incurred by the design and the load it must carry throughout its existence. It is not an overstatement to say that by creating the detail of his design to serve the economy of construction as well as the economy of operation, the designer may often reduce by 10 to 20 per cent the capital sunk forever in that most unwelcome of all entries, "construction labor."

SECTION XXXI

METHODS OF FINANCING

By Donald M. Liddell[1]

Introduction.—While there may be some question as to the propriety of this section in a chemical engineering handbook, the courses in college economics many times absolutely ignore the various types of security by which enterprises are financed, and since after all, the object of most engineering work is to give a return on these securities, they seem deserving of some notice.

While a privately owned company is in many respects an excellent thing, a successful enterprise usually outgrows one-man ownership, while there is always the chance that a failure will involve the owner's entire fortune. Therefore, both to limit individual liability, and to facilitate raising money, enterprises are usually incorporated. Those who take the chances of the business, the partners, are the stockholders, those who lend money at fixed rates (creditors) are the note and bond holders.

In discussing the various forms of corporate issues, illustrations have been given of many securities falling under the various classes, so that if further information is desired concerning a particular form of indenture, easy reference may be made to at least one illustrative type.

Common Stocks.—Theoretically the common stockholder is the ultimate owner of the business and (except in rare cases, such as the former American Brake Shoe & Foundry Co.'s organization) the profits of the business after payment of interest and guaranteed dividends accrue to him.

For purposes of control by an unchanged management over a period of several years the holders of the common stock often deposit their stock certificates in a so-called voting trust and receive instead *voting-trust certificates*, the trustees of the trust then having all the voting powers. There has been much debate as to whether voting trusts are consistent with public welfare, and most states now limit their life to 5 years.

The value of each share of stock may be assigned a definite value, its par value, the number of shares times this par value being the original theoretical value of the portion of the business belonging to the common stockholders. Or the shares may be of "no par value," each share merely representing a fraction of the ownership of the business, which is practically what all common stocks are. However, it often appears that a certain sale value is inherent in the phrase "par value, $100 per share" even though the entire $100 consists of capitalized aspirations, and the "no par value" idea does not make much headway.

Occasionally the common stock is split into "founders' shares" and "ordinary shares," the founders' shares, usually but few in number, taking a certain fixed percentage of the profits, or a fixed percentage of the profits[2] over a certain amount, giving them a return entirely incommensurate with that on the "ordinary shares," and often out of all proportion to any risk or responsibility assumed by the founders.

As an elementary principle, both of sound business and also of law, dividends may

[1] Weld & Liddell, Engineers and Economists, New York, N. Y.

[2] That is, of the profits accruing to the common stock.

not be paid by a company after such payment impairs the value of the common stock but may be paid from a previously earned surplus when there are no current earnings. Nevertheless, instances are not wanting where dividends have been paid from the proceeds of stock sales.

Preferred Stocks.—The name of course implies a certain preference over the common stock. This usually consists in a prior claim to the earnings until a given dividend is paid before anything may be paid on the common. The preference may end here, as it does with the 7 per cent preferred of the American Sugar Refining Co., or it may also include a prior claim on assets in event of dissolution, up to a given amount, usually par and accrued dividends, before the common stock receives anything.

But the preference on assets is limited only by the terms of the indenture, for the American Zinc, Lead & Smelting Co.'s preferred has a stated par of $25, but must be paid for at $100 if called. However, this contingency appears most remote.

Preferred stocks may be either cumulative or non-cumulative. In the first case, if the dividend is not earned and cannot be paid from a previously earned surplus it must be paid from later earnings before the common stock can receive anything. Examples of such payments were those of Republic Iron & Steel and Crucible Steel, which made up previous deficits on their preferred stock during the War. On the other hand a preferred stock may be non-cumulative and entitled only to fixed dividends that may properly be paid from earnings or surplus. In this case, if for any reason a dividend is not paid during any period, the stockholder receives nothing on this account later. Such preferred stocks are those of the Pressed Steel Car Co. and the Atlantic, Gulf & West Indies S. S. Co.

A preferred stock may be "participating." In this case, after payment of the guaranteed dividend on the preferred, and a stated dividend on the common, the preferred shares with the common in the further earnings.

Or the preferred stock may be entitled to all the earnings after a given amount has been paid on the common. For instance, the old preferred stock of the American Brake Shoe & Foundry Co. was entitled to 7 per cent before the common received anything, then the common received the benefit of the earnings until 7 per cent had been distributed on it, after which the preferred received the benefit of all the earnings.

But merely calling a stock "preferred" where no actual preference exists, does not make it so. Great Northern "preferred" is the only class of stock outstanding, and the name represents only the personal "preference" of the late J. J. Hill.

Two or more classes of preferred stock may be outstanding simultaneously. In this case their rights may be very simply related, as in the case of the Superior Steel Corporation, where the first preferred has prior claim over the second preferred both as to earnings applicable to dividends and as to assets in case of liquidation; the second preferred in turn having similar claims over the common, or the respective rights may be exceedingly complicated, as in the case of the Bethlehem Steel Corporation, where it appears that the 8 per cent cumulative preferred has prior claim on earnings, while the 7 per cent non-cumulative preferred would appear to be a lien prior to the 8 per cent in case of liquidation and distribution of assets.*

The case may be further complicated by the assumption of the liability for the dividends of the preferred stocks of other companies. Thus it appears that the preferred *A* and *B* stocks of the American Smelters Securities Co. all of whose common stock is owned by the American Smelting & Refining Co. are prior liens over the preferred stock of the latter corporation. The preferred *A* of the former appears to have first preference as to payment of dividends, but the preferred *B*, being guaran-

* This refers to the stocks of the former unmerged company.

teed by indorsement, probably has preference in regard to assets. Common stocks of controlled corporations where a given return is assured rank for all practical purposes with preferred stocks.

In order to facilitate the raising of money, other privileges than that of priority regarding dividends and assets are occasionally given to the purchasers of preferred stock. Thus, the preferred stock may be made convertible into common stock. In this way, if the company attains marked success, the preferred stockholders can exchange their stock for common and share in the prosperity of the common stockholders. The convertibility may be at any agreed ratio.

In the case of the Superior Steel Corporation's preferred stocks, already referred to, the preferred is exchangable for common share for share. In the case of the General Asphalt Co. one share of preferred is exchangable for 1½ shares of common. Further protection may be thrown about a preferred stock in order to increase its salability by stipulating that no mortgages (or none except purchase-money mortgages) may be created without the written consent of some determined percentage of the preferred stockholders.

Preferred stocks may or may not be retirable, and in the former case may be retirable in part, either by lot or by purchase by sinking fund. The U. S. Steel Corporations preferred stock may not be retired. That of the American Zinc, Lead & Smelting Co. may be retired only as a whole. The preferred *A* of the American Smelting Securities Co. is retirable by lot, a part each year. In these cases a sinking fund is set up by allotting a certain percentage of the earnings or a certain set amount from the earnings, or a certain set amount based on the preferred stock outstanding, and the stock either bought in by lot, or purchased in open market, or acquired by tender. In any case there is usually a premium given the holder of the stock if the stock is forcibly retired either in part by lot, or as a whole. Similar sinking funds are used to retire bonds. A case where all of an issue of bonds must be retired at 110 of face is that of the U. S. Steel Corporation's 10 to 60 year second-mortgage sinking-fund bonds of 1963.

Preferred stocks may have equal voting power with common, no voting power, or voting power only in case of default either in dividends or sinking funds. In the case of preferred stock without voting power, the rights of the stockholder differ but little from those of a holder of unsecured debentures, although the latter could probably force payment of interest if earned in a court of equity where the preferred stockholder might not be able to force the payment of dividends, even if earned.

Debenture has no definite legal meaning, except that it is always a debt.[1] It may be applied to any promise or security of the company to pay money. It may be a mere promise to pay, or a covenant under seal to pay, or a mortgage under the seal of the company.

In the United States, however, it is usually considered an unsecured credit obligation only and default in interest does not necessarily serve as a basis for legal proceedings. However, there may be a provision that if any mortgage be placed on the property after the creation of the debentures, the debentures shall then be equally secured with the new bonds. Such a provision appeared in the convertible debentures of the Baltimore & Ohio R. R. Co., due 1933. • •

Debentures may or may not be convertible. Those of the Alaska Gold Mines were convertible into common stock at $30 per share. Debentures are sometimes spoken of as "notes" or "bonds," according to whether the maturity is short or long, but there seems to be no justification for the term bonds in connection with them unless actually secured by mortgage deed of trust, in which case they cease to be debentures.

[1] Cook on "Corporations," Vol 1, Sec. 14.

The word "stock" has a peculiar meaning in England, referring to debentures as well as to share capital. Shares, bonds and debentures are of fixed amounts, but stock is issued in any amount or multiple of certain sums, usually £1.

Debenture stock is an English term also. It does not mean shares of stock, but means an English bond,[1] an absolute obligation of the company to pay principal and interest at fixed times. It is doubtful whether the debenture stock of the General Motors Corporation is correctly named, whereas the preferred stock of the S. S. Kresge Co. comes close to being such an obligation, except that the dividends must be earned before they can be paid.

Notes may be unsecured (debentures) or secured either by collateral trust or mortgage. In the last case the only difference between notes and bonds seems to lie in the names based on popular usage resting on the very indeterminate matter of short or long maturity, roughly obligations running 10 years or less being spoken of as notes. On the other hand, the mortgage deed of trust obligations of the Hanna Furnace Co., running only 5 years, are spoken of as bonds.

The security may be actual pledge of real property (mortgage notes), or the deposit if stocks or bonds of the issuing company or of other companies (collateral-trust notes), or they may be secured by indorsement of other individuals or corporations. In this latter case, an indorsement on each note or bond by the guaranteeing corporation is a better security than a guarantee merely stated in the general deed of trust. Bonds may even have two guarantors, as is the case with the 4½ per cent bonds of the Chicago, Lake Shore & Eastern Ry. (guaranteed by the U. S. Steel Corporation and the Elgin, Joliet & Eastern Ry.).

To make them attractive at the time of issue, conversion privileges may be given to notes and bonds, just as with stock. This is particularly done with the issues of mining and oil companies upon the theory that the investor in these issues takes a greater risk than does the ordinary industrial or railway-bond buyer and some means of giving him a speculative chance as well as his fixed return is necessary. For this reason the bonds or notes are usually made convertible into stock at some higher figure than the market price of the stock at the time of issue, so that the bond holder does not have so great a speculative chance as the original stockholder and yet has some chance for appreciation on his securities. Examples of this are the Chile Copper Co. 7's, each $1,000 bond convertible into 40 shares of stock at $25 per share; the Chile Copper Co. 6's, a later issue, convertible into stock at $35 per share; the General Asphalt Co. 8's, convertible into common stock at $100 per share.

The conversion privilege often is terminated before the maturity of the bond, in order not to give the holder too great a speculative chance. Such were the convertibles of the Erie R. R.

Income Bonds.—These are a half-way house between preferred stocks and true mortgages. The interest is payable only if earned, is usually, but not always cumulative, as in preferred stocks, but if the bonds are in default at maturity there is (usually) specific property that can be levied on, and the holder is, of course, legally a creditor and not a partner (stockholder). The income bond holder has no vote, but neither do some preferred stockholders. The Hudson & Manhattan Ry. Co's. adjustment income bond is a good example of this class of security.

Collateral-trust Bonds.—These are secured by deposit of stocks, notes or bonds with a trustee, rather than by pledge of real property. A bond may be both mortgage and collateral trust, as are the International Agricultural 5's of 1932.

[1] Cook on "Corporations."

Mortgage Bonds.—These are secured by the pledge of real property, and are supposedly the strongest form of security that can be given. Corporate mortgages are usually made in the form of a mortgage deed of trust, by which the bonds are secured, necessarily so if many bonds are to be issued. Of course if there is to be but one bond holder the mortgage may run to said holder, just as in individual mortgages.

As said above, the mortgage feature may be joined with collateral trust provisions, and may also be convertible into stock. They may cover only specific property owned by the debtor corporation at the time of issue, or they may cover "all property hereafter acquired," the latter clause usually being qualified by, "subject to purchase money mortgages."

In case a company has originally placed a first mortgage on its property, it may also place a second mortgage, which is a lien on the property of the company after and subject to the satisfaction of the first mortgage. A company may also issue so-called refunding mortgages, which are usually first liens on property acquired later than and not subject to the previously placed first mortgage, and which provide for bonds to be issued later to take the place of the first mortgage at maturity.

Commercial Paper.—This is a method of raising money available only to companies of recognized standing, and consists in placing notes with various banks through a broker. These notes run usually 3 months, and while it is the cheapest method of all to raise money in good times, it may leave the issuing firm stranded in bad ones. Usually commercial paper is not considered a good risk if the liquid assets (cash accounts and bills receivable, etc.) are not twice the current liabilities, including the paper issued.

Discounting Accounts Receivable.—Recently there has been a great growth of the so-called "credit companies." These advance money on the pledge of certain specific accounts receivable, backed by the general credit of the pledging firm. It is an expensive method of raising money, but is often of great service.

APPENDIX

METRIC—ENGLISH EQUIVALENTS

Length

1 ft. = 0.3048060096 m.
1 in. = 2.540005 cm.
1 m. = 3.28083 ft. = 39.370000 in.

Area

1 sq. in. = 6.452 sq. cm.
1 sq. ft. = 0.09290 sq. m.
1 sq. yd. = 0.83613 sq. m.
1 sq. m. = 1.1960 sq. yd. = 10.764 sq. ft.
1 sq. cm. = 0.15500 sq. in.

Volume

1 cu. yd. = 0.764559445 cu. m
1 cu. ft. = 0.028317 cu. m.
1 cu. in. = 16.3872 c.c.
1 cu. ft. = 0.028316 l.
1 cu. in. = 16.3867 ml.
1 cu. m. = 1.3079 cu. yd.
1 c.c. = 0.06102 cu. in.
1 l. = 61.025 cu. in. = 0 035315 cu. ft.

Mass

1 lb. (Avoirdupois) = 0.4535924277 kg.
1 oz. (Avoirdupois) = 28.3495 g.
1 oz. (Troy) = 31.10348 g.
1 dram (ʒ = 3 ℈, apoth.) = 3 887935 g.
1 kg. = 2.20462234 lb. (Avoirdupois) = 2.67923 lb. (Troy)
1 g. = 0.035274 oz. (Avoirdupois) = 0 032151 oz. (Troy)
= 15.4324 grains

Capacity

1 qt. (liquid) = 0.94633307 l.
1 qt. (dry) = 1.1012 l.
1 l. = 1.05671 qt. (liquid) = 0 9081 qt. (dry) = 33.8147 fl. oz.
1 fl. oz. = 0 0295729 l. = 1 80469 cu. in.

NOTE.—1 gal. (liquid) = 231.0 cu. in.
1 bu. (dry) = 2,150 42 cu. in.
1 l. = 1,000 027 c.c.

Temperature

$$°C. = \frac{5}{9}(°F. - 32)$$

$$°F. = \frac{9}{5}\,°C. + 32$$

Energy

1 hp.	= 0.746 kw. = 33,000 ft.-lb. per minute
1 kw.	= 1.341 hp. = 1,000 joules per second
1 ft.-lb.	= 1.383×10^7 ergs = 1.383 joules = 0.1383 kg.-m.
1 poundal	= 13,825 dynes.
1 gram's weight	= 980 dynes.
1 pound's weight	= 444,518 dynes.
1 hp. year	= 6,535 kw.-hr.
1 kw.-yr.	= 11,747 hp.-hr.

Many tables of constants will be found in the sections to which they particularly pertain. Among those to which particular attention is directed are:

Specific Gravity of Solids. Sec. I, p. 108.

Specific gravity, molecular weights, critical temperature and critical pressure of gases. Sec. IV, p. 144.

Specific heat of gases. Sec. IV, p. 146.

Specific gravity-Baumé-Brix conversion tables. Sec. X, pp. 397, 398.

Standard thermometric points, Sec. XII, p. 410.

Van der Waals' constants, Sec. IV, p. 190.

ALCOHOL PROOF

Percentage by weight	C_2H_5OH by volume	Specific gravity 60°F.	British proof	U. S. proof	Fiscal proof	Tralles' hydrometer
100 00	100	0 79389	+74.8	200	175 35	100
48.98	57	0.91999	proof	114	100 00	57
42.25	50	0.93426	−12 4	100	86.17	50

While the basis of U. S. proof is very readily understood, it has no historic justification. In former times, the smugglers "proved" their alcoholic spirits by pouring some over gunpowder and lighting the mass, if the gunpowder burned after the alcohol burned off the spirit was "over proof." If the gunpowder remained a sodden mass the spirit was "under proof." Unfortunately for those of centigrade mind, the dividing point did not come at exactly 50 per cent of alcohol by volume.

SOLUBILITIES OF SOLIDS IN WATER

S = number of grams of substance of the given formula, including water of crystallization, if that be given, which when dissolved in 100 g. of water makes a saturated solution at the temperature stated.

p = number of grams of anhydrous substance per 100 g. of saturated solution.

w = number of grams of substance as given by formula in 100 g. of water required to form a saturated solution.

Substance	0°C.	10°	15°	20°	40°	60°	80°	100°
Aluminum-potass. alum, $KAl(SO_4)_2 \cdot 12H_2O$, *S*	5.65	7.60	9.59	11.40	23.83	57.35	321.3	∞
chloride, $AlCl_3 \cdot 6H_2O$, *S**				400.0				
sulphate, $Al_2(SO_4)_3 \cdot 18H_2O$, *S**	86.85	96.8		107.35	167.6	262.6	467.3	1132.0
Ammonium alum, $NH_4Fe(SO_4)_2 \cdot 12H_2O$, *S**			33 3					
carbonate, $(NH_4)_2CO_3 \cdot H_2O$, *S*			100.0					
chloride, NH_4Cl, *S*	29 4	33 3	35.2	37.2	45.8	55.2	65.6	77 3
chloroplatinate, $(NH_4)_2PtCl_6$, *S*	0 666							12.5
nitrate, NH_4NO_3, *S*	118 3	147.1	171.9	191.4	297 0	421.0	580.0	871 0
oxalate, $(NH_4)_2C_2O_4$, *S*	2 215							
sulphate, $(NH_4)_2SO_4$, *S**	70.6	73.0	74 2	75.4	81.0	88.0	95.3	103.3
Arsenious acid, As_2O_3, *S*			1 657		2 93			6 0+
Barium chloride, $BaCl_2$, *S*	30.9[9]	33 3[9]	34 5[9]	35 7[9]	40.7[9]	46 4[9]	52.4[9]	58 8[9]
hydroxide, $Ba(OH)_2$, *S*	1 67[10]	2.48[10]	3.23[10]	3 89[10]	8 22[10]	20 94[10]	101.4[10]	
nitrate, $Ba(NO_3)_2$, *S*	5 0	7.0		9 2	14 2	20.3	27.0	34 2[7]
Boric acid, B_2O_3, *S*	1 1	1 5		2 25	3 95	6 2	9.5	15 52
Cadmium chloride, $CdCl_2$, *p*		51 6		52 7		57.7		
nitrate, $Cd(NO_3)_2$, *S*	109 7				159 2	326 9		
sulphate, $CdSO_4$, *S*	76 5[2]	76 0[2]	76 3[2]	76.6[2]	78 5[2]	83 7[2]	70 2[2]	60 77[2]
Calcium chloride, $CaCl_2$, *S*	59.5[8]	65 0[8]		74 5[8]		136 8[8]	147.0[8]	159 0[8]
hydroxide, $Ca(OH)_2$, *S**	0 185	0 176	0 170	0.165	0 141	0 116	0 94	0.077
hypochlorite, $Ca(OCl)_2 \cdot 4H_2O$	deliquescent, soluble							
nitrate, $Ca(NO_3)_2$, *p*				55 0				
sulphate, $CaSO_4$, *p*	0 1759	0.1928	0 2020	0 2096	0 2097			0 1619
Chromic anhydride, CrO_3, *p*	62 08		62 38					67 39
sulphate, $Cr_2(SO_4)_3 \cdot 18H_2O$, *S**				120 0				
Cobaltous chloride, $CoCl_2$	29 5[11]	31 5[11]		33 5[11]	41 0[11]	47 5[11]	80 0[11]	51 0[11]
sulphate, $CoSO_4 \cdot 7H_2O$, *S*	25 53	30 55	33 05	36 2	48 5	57 8[13]	69 8[13]	82 6[13]
Cupric chloride, $CuCl_2$, *p*	41 4	42 15		43 5	45 6	47 7	49 8	51 9
nitrate, $Cu(NO_3)_2$, *p*	45 00	48 79		55 58	61 51	64 17	67.51	77 59
sulphate, $CuSO_4$, *S*	14 3[12]	17 4[12]	18.8[12]	20 7[12]	28.5[12]	40 0[7]	55.0[12]	75 0[12]
Cuprous chloride, Cu_2Cl_2, *S*				1 50				
Ferric-ammon. sulphate, $NH_4Fe(SO_4)_2 \cdot 12H_2O$, *S**			33 3					
chloride, $FeCl_3$, *S*	74 39			91.85		372.8	52 59	535.8
nitrate, $Fe(NO_3)_3 \cdot 9H_2O$	deliquescent, soluble							
Ferrous chloride, $FeCl_2$, *p*		39 2		40 0	43 6	47.0	50.0	51.4
nitrate, $Fe(NO_3)_2$, *p*	41 53			45 5		62 5		
sulphate, $FeSO_4$, *S*	7 9	16 2	20 4	33 5	42 6	61 7	62.3	42.6
Gold bromide, $AuBr_3$	Slightly soluble	Aurous bromide, AuBr, is insoluble.						
(auric) chloride, $AuCl_3$, *S*	Deliquescent	67.0 Aurous chloride slowly decomp by H_2O.						
(aurous) cyanide, $Au(CN)$	Insol H_2O, alcohol, ether. Sol. in NH_4OH or sol. cyanides.							

* The formulas marked * are those of the solid phases that are in equilibrium with the solution. The figures are mainly from Seidells' "Solubilities of Inorganic and Organic Substances." D. Van Nostrand Co., New York.

Lead acetate, $Pb(C_2H_3O_2)_2$, *S*				40.0				200.0
chloride, $PbCl_2$, *S*	0.6728		0.9070				2 622	3.342
nitrate, $Pb(NO_3)_2$, *S*	37.65	46.35		54.4	72.2	91.5	111.3	132.9
sulphate, $PbSO_4$, *S*		0.0031	0.0041	very sol. in ammonium acetate.				
Lithium carbonate, Li_2CO_3, *S**	1.54	1.43	1.38	1.33	1.17	1.01	0.850	0.720
chloride, LiCl, *S*	67.0	72.0	75.0	78.5	90.5	103.0	115.0	127.5
Magnesium chloride, $MgCl_2$, *S*	52 8[14]	53.5[14]		54.5[14]	57.5[14]	61.0[14]	66.0[14]	73.0[14]
sulphate, $MgSO_4$, *S*	26.9	31.5	33.8	36 2	45 6	55.0	64.2	73.8
Manganous chloride, $MnCl_2$, *S*	63.4[5]	68.1[15]		73 9[15]	88.6[15]	108.6[15]	112.7[15]	115.3[15]
sulphate, $MnSO\cdot4H_2O$, *S*	55.4	61.1	63.8	66.3	73.1	65.9	61.5	52.9
Mercuric chloride, $HgCl_2$, *p*	3.5	4 5	5.0	5 4	9.3	14.0	23.1	38.0
Mercurous chloride, Hg_2Cl_2, *S*			0 0002					
Nickel. ammon. sulphate, $(NH_4)_2Ni(SO_4)_2\cdot6H_2O$, *S*		3.2		5.9	11.5	17.0		
Nickelous chloride, $NiCl_2$, *p*	35 0	37.3		39.1	42 3	45.1		46.7
nitrate, $Ni(NO_3)_2$, *p*	44 3			49.1		62.0		
sulphate, $NiSO_4$, *S*	30 0			39.7	49 0	57.2		
Oxalic acid, $(CO\cdot OH)_2$, *S*	3.45	5.55		8 78	21.15	45 55		
Potassium alum, $AlK(SO_4)_2\cdot12\ H_2O$, *S**	5 65	7.60	9.59	11.40	23 83	57 35	71.0	
bicarbonate, $HKCO_3$, *S*	22.4	27.7		33 2	45 3	60 0		
bichromate $K_2Cr_2O_7$, *p*	5.0	7.0		12.0	26.5	45.0	65.5	88.5
bromide, KBr, *S*	53 5	59.5	62.5	65 2	75.5	85 5	95.0	104.0
carbonate, K_2CO_3, *S*	89 4	109.0	...	112 0	117.0	127.0		136.0
chlorate, $KClO_3$, *S**	3 3			7.4	13.8	24 0	37.7	56.5
chloride, KCl, *S**	27.6	31.0	32 4	34 0	40 0	45 5	51.1	56.7
chromate, K_2CrO_4, *p*	59 3	61.2	...	63 2	67.0	71 0	75.0	79.0
ferricyanide, K_3FeCy_6, *S*	31 0	36.0	...	43 0	60 0	66.0		82.0
ferrocyanide, K_4FeCy_6, *S*	13 0	20 0		32.0	54 0	67.0		82.0
hydroxide, $KOH\cdot2\ H_2O$, *S**	97.0	103 0	107 0	112 0	138.0[3]			178.0[3]
iodide, KI, *S**	127 5	136 0	140 0	144 0	160 0	176.0	192 0	208.0
nitrate, KNO_3, *S**	13 3	29.9	25 8	32 0	64 0	110.0	169.0	246.0
permanganate, $KMnO_4$, *S**	2 83			6 40	12 56			
sulphate, K_2SO_4, *S*	8.5	9.7	10.3	10 9	14.0	17.8	21.8	26.2
sulphite, K_2SO_3, *S*	100 0 somewhat deliquescent							
Silver nitrate, $AgNO_3$, *S**	122 0	170.0	196.0	222 0	376.0	525.0	669.0	952.0
Sodium acetate, $NaC_2H_3O_2$, *S*	34 0	41.0		49.0	65.0			
arsenite, Na_3AsO_3	very sol. water. Insol. in ethyl acetate. Does not crystallize.							
alum, $NaAl(SO_4)_2\cdot12H_2O$, *S**	110 0							
bicarbonate, $HNaCO_3$, *S*	6 9	8.15		9.6	12.7	16 4		
bisulphate, $HNaSO_4$, *S*	...			25 0				50.0
borate, $Na_2B_4O_7$, *S*	...	1.6		2 8	6.3	19.4	31.5	52.5
bromide, NaBr, *S*	72.7	78.0		83.6	96.9	114.5	116.0	117.5
carbonate, $Na_2CO_3\cdot10H_2O$, *S**	7.0	12.5	16.4	21.5	46.1[4]	46.0[4]	45.8[4]	45.5[4]
chloride, NaCl, *S**	35.7	35.8	35.9	36.0	36 6	37.0	38.0	39.0
hydroxide, NaOH, *S*	42.0	51 5		109.0	129.0	174.0	313.0	34.0
iodide, NaI, *S*	158 7	168 6		178.7	205.0	256.8	296.0	302.0
nitrate, $NaNO_3$, *S*	72.9	80.6		87.7	103.4	123.0	148.0	177.9
sulphate, Na_2SO_4, *S*	4 8	9.0	13 4	19.5	49.0[5]	45.3[5]	43.7[5]	42.5[5]
sulphate, $Na_2SO_4\cdot10H_2O$, *S*	12 17	23.04	35 96	58.85	∞	∞		

Substance	0°C	10°	15°	20°	40°	60°	80°	100°
Strontium chloride, $SrCl_2$, *S*	43.0[6]	48.0[6]	50.0[6]	53.0[6]	65 0[6]	82.0[6]	91.0[6]	101.0[6]
hydroxide, $Sr(OH)_2 8H_2O$, *p**	0 90	1 23	...	1.74	3 83	7.88	17.42	53.20
nitrate, $Sr(NO_3)_2$, *S*	39 5	54 9		70.8	91.3	94 0	97.2	101.1
Stannous Chloride, $SnCl_2$, *S.*	83 9		269.8					
Sugar, $C_{12}H_{22}O_{11}$, *S*..	179 2	190.5	197 0	203 9	238.1	287.3	362.1	487 2
Tartaric acid $C_2H_2(OH)_2(COOH)_2$, *S*	115 0	125.7		139.4	176 0	217.6	273 3	343 4
Zinc chloride, $ZnCl_2$, *S*			..	..	452 0	488 0	543.0	615 0
nitrate, $Zn(NO_3)_2$, *p*	48 66	51.33	52 75	54 2	67 4			
sulphate, $ZnSO_4$, *S*.	41.93	47 6	50 9	. .	70 5	82 7	86.6	80 8

* The formulas marked * are those of the solid phases that are in equilibrium with the solution. The figures are mainly from Seidells' "Solubilities of Inorganic and Organic Substances." D Van Nostrand Co . New York

[2] Solid phase becomes $CdSO_4 \cdot H_2O$ at 74°C , below that it is $CdSO_4 \cdot \frac{2}{3}H_2O$

[3] Solid phase becomes $KOH \cdot 3\frac{1}{2}H_2O$ at 32 5°C., and KOH H_2O at 50°.

[4] Solid phase becomes Na_2CO_3 H_2O at 35°C.

[5] Solid phase becomes Na_2SO_4 at 32 38°C , below that is Na_2SO_4 $10H_2O$.

[6] Solid phase becomes $SrCl_2 \cdot 2H_2O$ about 63° C , Below that it is $SrCl_2$ $6H_2O$.

[7] A saturated solution at 215°C. contains 84 5 g. $Ba(NO_3)_2$ in 100 g. water.

[8] Solid phase is $CaCl_2 \cdot 6H_2O$ up t 30.2°. At and above 60° it is $CaCl_2 \cdot 2H_2O$

[9] The solid phase in equilibrium with the solution is $BaCl_2$ 2 H_2O.

[10] The solid phase in equilibrium is $Ba(OH)_2 \cdot 8H_2O$.

[11] Below 35°C, the solid phase is $CoCl_2$ $6H_2O$, above 35° it is $CoCl_2$ H_2O.

[12] The solid phase in equilibrium with the water is $CuSO_4 \cdot 5H_2O$.

[13] These solubilities are for anhydrous $CoSO_4$.

[14] Solid phase in equilibrium with water, $MgCl_2$ $6H_2O$

[15] Solid phase in equilibrium with water below 60°, $MnCl_2 \cdot 4H_2O$; above 60°, $MnCl_2 \cdot 2$ H_2O

INTERNATIONAL ATOMIC WEIGHTS, 1922

Element	Symbol	Weight	Valence[1]	Electrochem. equivalents, g. per amp.-hr.	Melting points, deg. C.	Boiling points deg. C., visible ebullition
Aluminum	Al	27.0	3	0.3354	658.7	1800.0
Antimony	Sb	120 2	3	1.4949	630.0	1460.0
Argon	A	39.9	0		−189.3	−186.0
Arsenic	As	74.96	3	0 9324	850.0	450.0[2]
Barium	Ba	137.37	2	2.5619	850.0	
Bismuth	Bi	209 0	3	2.5992	271.0	1440.0
Boron	B	10 9	3		2350 0	3500[2]
Bromine	Br	79.92	1	2.9814	−7.3	58.75
Cadmium	Cd	112 40	2	2.0955	320 9	778.0
Caesium	Cs	132.81	1		26 0	
Calcium	Ca	40.07	2	0 7477	810 0	
Carbon	C	12.05	4	0.1118	>3600.0	3700.0
Cerium	Ce	140 25	4		623.0	
Chlorine	Cl	35 46	1	1 3230	−101 5	−37.6
Chromium	Cr	52.0	3	0 6476	1520 to>Fe	2200.0
Cobalt	Co	58 97	2	1.1000	1610[3]	
Columbium	Cb	93 1	5		1950–2200	
Copper	Cu	63 57	2	1.1858	1083.0	2100 0
Dysprosium	Dy	162.5				
Erbium	Er	167.7				
Europium	Eu	152 0				
Fluorine	F	19.0	1	0.7085	−223.0	−187.0
Gadolinium	Gd	157.3				
Gallium	Ga	70 1			30 1	
Germanium	Ge	72.5			958.0	
Glucinum	Gl	9.1			1280.0	
Gold	Au	197.2	3	2.4524	1063.0	2100 0
Helium	He	4.002	0		−271.9	−268.8
Holmium	Ho	163.5				
Hydrogen	H	1.008	1	0.03764	−259.0	−252.8
Indium	In	114.8			154.5	1000.0
Iodine	I	126.92	1	4 7353	114 0	184 35
Iridium	Ir	193 1	4		2300 0	2850.0
Iron	Fe	55 84	2	1.0416	1530±5	2450.0
Krypton	Kr	82.92			−169.0	−151.7
Lanthanum	La	139.0			810 0	
Lead	Pb	207.20	2	3.8654	327.4	1525.0
Lithium	Li	6 94	1	0.2622	186.0	500 0
Lutecium	Lu	175 0				
Magnesium	Mg	24.32	2	0.4531	651.0	1120.0
Manganese	Mn	54.93	2	1.0255	1260±20	1900 0
Mercury	Hg	200.6	2	7.4840	−38.87	357.0
Molybdenum	Mo	96.0	2	1.7900	2550 0	3350.0
Neodymium	Nd	144.3			840 0	
Neon	Ne	20.0	0		−253.0	−245.9

[1] In those cases in which a metal has two valences, the valence given corresponds to the electrochemical equivalent, and may not necessarily be the commoner one.

[2] Sublimes. [3] Commercial metal, about 1480° C.

INTERNATIONAL ATOMIC WEIGHTS, 1922.—*Continued*

Element	Symbol	Weight	Valence[1]	Electrochem. equivalents, g per amp.-hr.	Melting points, deg C.	Boiling points deg. C. visible ebullition
Nickel	Ni	58.68	2	1.0946	1452±3	2450.0
Niton	Nt	222.4	0		−71 0	−62.0
Nitrogen	N	14.008	3	0.1742	−210.5	−195.7
Osmium	Os	190.9	..		2700.0	2950 0
Oxygen	O	16.00	2	0.2985	−218.0	−183 0
Palladium	Pd	106.7	2	1.9951	1550.0	2540 0
Phosphorus	P	31.04	..		44.1	287 0
Platinum	Pt	195.2	4	1.8206	1755.0	2650 0
Potassium	K	39.10	1	1.4584	62.3	667.0
Praseodymium	Pr	140.9			940.0	
Radium	Ra	226.0	2		900.0	
Rhodium	Rh	102.9	.		1940.0	2750 0
Rubidium	Rb	85 45	.		38 0	696 0
Ruthenium	Ru	101.7	...	.	>1950.0	2780.0
Samarium	Sa	150.4	.	.	1350.0	..
Scandium	Sc	45.1	..		1200 0(?)	..
Selenium	Se	79.2	2	1.477	218.5	690.0
Silicon	Si	28.1	4	0.2638	1420.0	3800.0
Silver	Ag	107.88	1	4.0258	961.0	1955.0
Sodium	Na	23.00	1	0.8582	97.5	742.0
Strontium	Sr	87.63	2	1.6333	>Ca<Ba	
Sulphur	S	32.06	2	0.5980	112 8−119.2	444 5
Tantalum	Ta	181.5			2850.0	..
Tellurium	Te	127.5	2	2.379	451.0	1390.0
Terbium	Tb	159.2				.
Thallium	Tl	204.0	..	..	302.0	1700.0[2]
Thorium	Th	232 15	..		>1700.0<Pt	..
Thulium	Tm	169.9				
Tin	Sn	118.7	2	2.2144	231.9	2270.0
Titanium	Ti	48.1	4	0.4490	1795.0±15.0	2700.0
Tungsten	W	184.0	6	1.1437	3267.0	3700.0
Uranium	U	238.2	.		Near Mo.	3100.0
Vanadium	V	51.0	..	...	1720.0±20.0	..
Xenon	Xe	130.7	0	.	−140 0	−109.1
Ytterbium	Yb	173.5	...	.	1800.0(?)	..
Yttrium	Yt	89.33	.	.	1490.0	..
Zinc	Zn	65.37	2	1.2192	419.4	918.0
Zirconium	Zr	90.6			1700.0(?)	..

NOTE.—In addition to the above elements, there is some reason to believe in the existence of a gas "cornium" (so called from its existence in the solar corona) which would form 0 00058 per cent. of the earth's atmosphere according to DR. A. WEGENER'S calculations (*Science*, Oct 31, 1913).

[1] In those cases in which a metal has two valences, the valence given corresponds to the electrochemical equivalent, and may not necessarily be the commoner one. [2] Also given as 1280° C.

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